

U.S. Department of the Interior  
U.S. Geological Survey

# **Total Mercury and Methylmercury in Fish Fillets, Water, and Bed Sediments from Selected Streams in the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998–2001**

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## FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

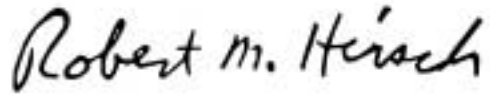
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/nawqamap.html>). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings (<http://water.usgs.gov/nawqa/natsyn.html>).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

A handwritten signature in black ink that reads "Robert M. Hirsch". The script is fluid and cursive, with the first letters of each word being capitalized and prominent.

Robert M. Hirsch  
Associate Director for Water

## CONTENTS

	Page
Foreword . . . . .	iii
Abstract . . . . .	1
Introduction . . . . .	2
Description of study area . . . . .	3
Acknowledgments . . . . .	3
Methods . . . . .	3
Fish, streamwater, and bed-sediment sampling . . . . .	3
Fish, streamwater, and bed-sediment laboratory analysis procedures . . . . .	7
Quality control . . . . .	8
Data analysis . . . . .	8
Distribution and concentrations of total mercury and methylmercury . . . . .	8
Patterns of distribution . . . . .	8
Concentrations . . . . .	12
Human-health and wildlife criteria . . . . .	13
Factors affecting concentrations . . . . .	13
Fish fillets . . . . .	15
Streamwater . . . . .	16
Bed sediment . . . . .	16
Differences among land-use groups . . . . .	19
Comparison of results with the National Mercury Pilot Program and other studies . . . . .	22
Summary and conclusions . . . . .	24
References cited . . . . .	26
Appendix . . . . .	29

## ILLUSTRATIONS

Page

Figure 1. Map showing sites sampled for mercury in fish, streamwater, and bed sediment in the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001. ....	4
2-4. Maps showing:	
2. Distribution of mercury concentrations in fish fillets within the Delaware River Basin. ....	9
3. Distribution of mercury and methylmercury concentrations in streamwater within the Delaware River Basin ....	10
4. Distribution of mercury and methylmercury concentrations in bed sediment within the Delaware River Basin ....	11
5-17. Graphs showing:	
5. Relation between mercury concentrations in smallmouth bass fillets and latitude within the Delaware River Basin ....	12
6. Mercury concentrations in fish fillets, U.S. Environmental Protection Agency human-health criteria, and U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria compared with land-use categories within the Delaware River Basin. ....	13
7. Relation between total mercury concentrations in smallmouth bass fillets and total mercury concentrations in bed sediment within the Delaware River Basin. ....	16
8. Relation between total mercury concentrations in smallmouth bass fillets and estimated population density within the Delaware River Basin. ....	16
9. Relation between population density and total mercury concentrations in streamwater samples within the Delaware River Basin. ....	17
10. Relation between population density and methylmercury concentrations in streamwater samples within the Delaware River Basin. ....	17
11. Relation between population density and methylation efficiency in streamwater samples within the Delaware River Basin. ....	18
12. Relation between population density and total mercury concentrations in bed-sediment samples within the Delaware River Basin. ....	18
13. Relation between population density and methylmercury concentrations in bed-sediment samples within the Delaware River Basin ....	18
14. Relation between methylmercury concentrations in bed-sediment samples and wetlands within the Delaware River Basin. ....	18
15. Relation between population density and methylation efficiency in bed-sediment samples within the Delaware River Basin. ....	19
16. Distribution of total mercury concentrations in smallmouth bass fillets by land-use groups within the Delaware River Basin ....	20
17. Distribution of streamwater and bed sediment forms of mercury (A) total mercury, (B) methylmercury, and (C) methylation efficiency, by land-use groups within the Delaware River Basin ....	21

## TABLES

	Page
Table 1. Sites where fish fillets, streamwater column, and bed-sediment samples were collected in the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	5
2. A summary of mercury concentrations in fish fillets and exceedances of the U.S. Environmental Protection Agency human-health criteria, and the U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria from selected sites in the Delaware River Basin, 1998 through 2001 . . . . .	14
3. Results of Spearman rank correlation analysis between mercury concentration in smallmouth bass ( <i>Micropterus dolomieu</i> ) fillets and environmental and landscape variables for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	15
4. Results of Spearman rank correlation analyses between environmental and landscape variables and mercury in streamwater samples for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	17
5. Results of Spearman rank correlation analyses between environmental and landscape variables and mercury in bed-sediment samples for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	19
6. Results of Kendall Tau correlation analyses among forms of mercury in fish fillets, streamwater, and bed-sediment samples, and environmental and landscape variables, within forested/low intensity-agricultural, agricultural, and urban land-use classes for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	22

## APPENDIX

Appendix. Site information, sampling years, fish species, number of fish per sample, mercury and (or) methylmercury concentrations in fish, streamwater, and bed sediment, and Loss-On-Ignition for bed sediment for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001 . . . . .	29
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## CONVERSION FACTORS, DATUMS, AND ABBREVIATED WATER-QUALITY UNITS

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
	<u>Length</u>	
inch (in)	2.54	centimeter
foot (ft)	0.3048	meter
	<u>Area</u>	
square mile (mi <sup>2</sup> )	2.590	square kilometer
	<u>Temperature</u>	
degree Fahrenheit (°F)	°C=5/9 (°F-32)	degree Celsius

Abbreviated water-quality units used in report:

g, gram  
cm, centimeter  
m, meter  
mm, millimeter  
ng/L, nanogram per liter (ppb, parts per billion)  
ng/g, nanogram per gram (ppt, parts per trillion)  
µg/g, microgram per gram (ppm, parts per million)

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88); horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).



# TOTAL MERCURY AND METHYLMERCURY IN FISH FILLETS, WATER, AND BED SEDIMENTS FROM SELECTED STREAMS IN THE DELAWARE RIVER BASIN, NEW JERSEY, NEW YORK, AND PENNSYLVANIA, 1998–2001

by Robin A. Brightbill, Karen Riva-Murray, Michael D. Bilger, and John D. Byrnes

## ABSTRACT

Within the Delaware River Basin, fish-tissue samples were analyzed for total mercury (tHg). Water and bed-sediment samples were analyzed for tHg and methylmercury (MeHg), and methylation efficiencies were calculated. This study was part of a National Mercury Pilot Program conducted by the U.S. Geological Survey (USGS). The Delaware River Basin was chosen because it is part of the USGS National Water-Quality Assessment Program that integrates physical, chemical, and biological sampling efforts to determine status and trends in surface-water and ground-water resources.

Of the 35 sites in the study, 31 were sampled for fish. The species sampled at these sites include smallmouth bass (*Micropterus dolomieu*), the target species, and where smallmouth bass could not be collected, brown trout (*Salmo trutta*), chain pickerel (*Esox niger*), largemouth bass (*Micropterus salmoides*), and rock bass (*Ambloplites rupestris*). There were a total of 32 fish samples; 7 of these exceeded the 0.3 µg/g (micrograms per gram) wet-weight mercury (Hg) concentration set for human health by the U.S. Environmental Protection Agency and 27 of these exceeded the U.S. Fish and Wildlife Service criteria of 0.1 µg/g wet weight for the protection of fish-eating birds and wildlife.

Basinwide analysis of Hg in fish, water, and bed sediment showed tHg concentration in fillets correlated positively with population density, urban land cover, and impervious land surface. Negative correlations included wetland land cover, septic density, elevation, and latitude. Smallmouth bass from the urban sites had a higher median concentration of tHg than fish from agricultural, low intensity-agricultural, or forested sites. Concentrations of tHg and MeHg in water were higher in samples from the more urbanized areas of the basin and were positively correlated with urban-

ization and negatively correlated with forested land cover. Methylation efficiency of water was negatively correlated with urbanization. Bed-sediment patterns were similar to those observed in water. Concentrations of tHg were higher in samples from the urbanized areas. In the more forested areas, MeHg concentrations were higher than in other land-use areas. Concentrations of tHg in bed sediment were positively correlated with urbanization factors (population, urban land cover, and impervious land surface) and negatively correlated with forested land cover and elevation. Forested land cover and latitude were positively correlated with concentrations of MeHg. The methylation efficiency was higher in samples from the forested areas and was negatively correlated with urbanization.

Analyses within land-use groups showed that tHg concentrations in fish fillets from the urban sites were positively correlated with forested land cover and wetland cover. Urbanization factors within the agricultural group were positively correlated with tHg in fish; concentrations of tHg in fish from sites in the low intensity-agricultural group were negatively correlated with urbanization factors. Within the agricultural land-use group, tHg concentrations in water were negatively correlated with septic density, and MeHg concentrations were negatively correlated with elevation. In the forested and low intensity-agricultural groups, MeHg in water was negatively correlated with forested and agricultural land cover. Methylation efficiency in water also was negatively correlated with forested land cover but positively correlated with agricultural land cover. Bed sediment concentrations of tHg in the forested and low-agricultural groups were positively correlated with agricultural land cover and negatively correlated with forested land cover. Concentrations of MeHg in bed sediment were positively correlated with septic density and drainage area

and negatively correlated with forested land cover. Methylation efficiency was negatively correlated with population density, agricultural land cover, and sulfate concentrations in water.

An urbanization effect was observed in all three media—fish, water, and bed sediment. Different factors, basinwide and within land-use groups, showed a complex relation. Additional sampling within these land-use groups could help characterize interrelations of Hg in the environment to fish in the Delaware River Basin.

## INTRODUCTION

Mercury (Hg) is a naturally occurring metal found primarily in cinnabar (mercurysulfate) that is released through the weathering of rock and (or) volcanic activity (National Research Council, 2000). However, the main source of Hg in the environment is from human activity through coal-combustion electrical power generation and industrial waste disposal (National Research Council, 2000; Stahl and Sobat, 2000). Environmental concentrations can be influenced by proximity to point sources such as sewage treatment plants and industrial discharges, and by geographic and physiographic factors that affect vulnerability to atmospheric deposition. Once Hg is released to the environment, it can be converted to a biologically toxic form of methylmercury (MeHg) by microorganisms found in soil and in the aquatic environment (National Research Council, 2000). MeHg is a potent neurotoxin that affects the central nervous system causing neurological damage, mental retardation, blindness, deafness, kidney malfunction, and, in some cases, death (National Research Council, 2000).

Methylation of Hg is of concern because MeHg is absorbed easily into the food chain (U.S. Environmental Protection Agency, 1997). MeHg readily crosses biological membranes and can accumulate to harmful concentrations in the exposed organism and biomagnify up the food chain (Krabbenhoft and others, 1999). This biomagnification can cause high levels of Hg in top predator fishes and have a detrimental effect on humans and fish-eating wildlife (Krabbenhoft and others, 1999; National Research Council, 2000).

The United States, along with other industrialized countries, has taken action to reduce Hg pollution; however, these reductions are not yet reflected in the air, soil, water, or fish (U.S. Environmental Protection Agency, 2001a). As of 1999,

41 states had fish Hg advisories (limits on numbers of meals consumed by humans per month). Of these 41 states, 11 have statewide Hg advisories for lakes and streams (U.S. Environmental Protection Agency, 2000a), particularly in the northeastern United States (Bahnick and Sauer, 1994).

The Delaware River Basin, located in the northeastern part of the United States, is included in the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. NAWQA is a long-term effort designed to evaluate the status of, and trends in, the quality of surface- and ground-water resources in the United States through an integrated approach of physical, chemical, and biological factors (Hirsch and others, 1988; Leahy and others, 1990; Gurtz, 1994; Gilliom and others, 1995). The NAWQA Program was designed to be conducted in more than 50 separate river basins and aquifer systems that account for about two-thirds of the water use and public water supply in the United States (Leahy and Wilber, 1991). These basins constituted the framework for regional- and national-level assessments such as the National Mercury Pilot Program (NMPP) (Brumbaugh and others, 2001).

The Delaware River Basin NAWQA study examined factors affecting Hg concentrations in samples of fish, water, and bed sediment and is part of the USGS NMPP. Factors examined included water quality and environmental and landscape conditions (Krabbenhoft and others, 1999; Brumbaugh and others, 2001). The national study proposed a national tHg bioaccumulation model (Brumbaugh and others, 2001) and recommended additional research in urban areas and within various regions. Additional research is necessary to determine the applicability of the national model for different geographic regions of the country and to examine factors within each region that cause deviations in the model.

This report (1) documents the occurrence and distribution of total mercury (tHg) and MeHg in game-fish tissue, water, and bed sediment in the Delaware River Basin, and (2) examines the relations among the three media and with environmental factors and watershed characteristics. Concentrations of tHg and MeHg also are compared to results from the NMPP. Any exceedances of the U.S. Environmental Protection Agency (USEPA) human-health criteria or the U.S. Fish and Wildlife Service's fish-eating bird and wildlife criteria are noted.

### **Description of Study Area**

The Delaware River Basin drains approximately 12,700 mi<sup>2</sup> and includes parts of Pennsylvania (6,460 mi<sup>2</sup>), New Jersey (2,970 mi<sup>2</sup>), New York (2,360 mi<sup>2</sup>), and Delaware (968 mi<sup>2</sup>) (fig. 1) (Fischer, 1999). The entire basin, except for the Coastal Plain Physiographic Province and the tidal part of the estuary, are part of the NAWQA study area. The population of the study area, as determined by the 1990 census, is over 7 million people (Fischer, 1999). The Delaware River originates in the Catskill Mountains of New York and flows southward and eventually flows into the Atlantic Ocean. The Lehigh and Schuylkill Rivers in Pennsylvania are major tributaries of the Delaware River.

The Delaware River flows through five physiographic provinces, from the Appalachian Plateau in the north, through the Valley and Ridge, the New England, the Piedmont, and the Coastal Plain in the south (fig. 1). Land use in the basin is about 60 percent forested, 24 percent agricultural, 9 percent urban/residential, and 7 percent surface-water bodies and miscellaneous land uses (Fischer, 1999). In the forested northern half of the basin, which is mostly within the Appalachian Plateau Physiographic Province, altitudes range from about 1,000 ft to greater than 3,000 ft. This area includes the Catskill Mountains and the town of Port Jervis, N.Y. Major cities in the Valley and Ridge Physiographic Province include Stroudsburg, Easton, Allentown, and Reading, Pa. No major cities within the study area are in the New England Physiographic Province.

The population density is highest in the urbanized south, primarily in the Piedmont (Trenton, N.J., and Philadelphia and Chester, Pa.) and Coastal Plain (Camden, N.J., and Wilmington, Del.) Physiographic Provinces, where the altitudes generally are below 330 ft. These provinces cover about 40 percent of the total study area, contain over 80 percent of the population, and have about 40 percent urban land cover and less than 45 percent forest land cover (Fischer, 1999).

During the 1998 through 2001 data-collection period, precipitation was below normal by 1 to 4 in., and streamflows were near the 7-day, 10-year low-flow values. In particular, 1999 was an extremely dry year, and all four basin states declared drought emergencies. However, in September 1999, Hurricane Floyd provided relief by dropping considerable amounts of rain across the

basin. The extreme conditions observed in 1999 were not experienced in the other years of this study.

### **Acknowledgments**

Many colleagues have contributed to this report, including USGS personnel who collected samples: Jeffrey Fischer, Ward Hickman, Jonathan Klotz, Timothy Oden, Susan Edwards, Paul Dunn, Kimberly Orlick, Gretchen Wall, and Brett Boehlert. We thank Michael Boyer and Richard Spear from the Pennsylvania Department of Environmental Protection and Steven Schubert from the U.S. Fish and Wildlife Service for their assistance in collecting data; David Krabbenhoft (USGS) and Mark Olsen (USGS) for their technical assistance; William Brumbaugh (USGS), Stephen Smith (USGS), and Barry Mower (Maine Department of Environmental Protection) for their review of the manuscript; and Kim Otto, James Bubb, Terriann Preston, and Leona McLanahan for helping to complete this report.

### **METHODS**

Within the Delaware River Basin, a total of 35 sites were sampled for a combination of either fish tissue, streamwater, and (or) bed sediments (table 1, fig. 1). Sites were selected to represent watersheds dominated by agricultural, forested, and urban land uses throughout much of the study area, and to include mixed land-use watersheds and several large-river (integrator) sites draining major parts of the Delaware River Basin. Most sites were in the more highly populated southern half of the study area. Basins upstream from sampling sites were characterized for land use and population density. Basins were delineated using 10 m digital-elevation data. Land-use data from 1992 Landsat Satellite Thematic Mapper Imagery and population data from 1990 United States census data and 1997 estimates were then applied to each basin (Fischer, 1999).

### **Fish, Streamwater, and Bed-Sediment Sampling**

Fish specimens were collected from 31 sites, streamwater samples from 25 sites, and bed-sediment samples from 30 sites. Because the same species of fish could not be collected at all sites, five different species were collected among the 31 sites. Smallmouth bass were collected at 21 of the 31 sites. Water and bed-sediment samples were collected at 16 of the 21 smallmouth bass sites. These 16 sites were used for the analysis.



**Table 1.** Sites where fish filets, streamwater column, and bed-sediment samples were collected in the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

Map locator number (fig. 1)	Site name	U.S. Geological Survey identification number	Latitude	Longitude	Drainage area (square miles)	People per square mile <sup>1</sup>	Land-use characteristics				
							Percent forest <sup>2</sup>	Percent agriculture <sup>2</sup>	Percent urban <sup>2</sup>	Percent impervious surface <sup>2</sup>	Land-use designation
1	Raccoon Creek near Swedesboro, N.J.	01477120	39°44'28"	75°15'33"	25.7	242	27.3	63.6	4.2	4.3	Agricultural
2	Cooper River at Haddonfield, N.J.	01467040	39°54'11"	75°01'19"	17.5	2,414	24.9	7.5	56.9	38.2	Urban
3	Darby Creek near Darby, Pa.	01475510	39°55'44"	75°16'22"	38	3,353	37.8	7.2	51.4	32.6	Urban
4	Ridley Creek near Media, Pa.	01476470	39°55'57"	75°24'42"	27.5	734	59.2	28.5	11.4	8.0	Mixed
5	South Branch Pennsauken Creek at Cherry Hill, N.J.	01467081	39°56'30"	75°00'05"	8.8	3,088	14.8	12.5	66.2	41.2	Urban
6	Schuylkill River at Philadelphia, Pa.	01474500	39°58'04"	75°11'20"	1,886	684	48.3	37.8	9.9	9.9	Integrator
7	North Branch Rancocas Creek at Pemberton, N.J.	01467000	39°58'10"	74°41'05"	113	388	63.4	3.9	7.6	9.5	Mixed
8	Crum Creek at Goshen Road near Whitehorse, Pa.	01475845	39°59'24"	75°26'16"	13	915	59.7	20.4	17.4	11.3	Mixed
9	Darby Creek at Foxcroft, Pa.	01475430	39°59'45"	75°21'21"	16.2	1,692	50.2	12.7	35.2	21.4	Urban
10	Wissahickon Creek below Walnut Lake near Manayunk, Pa.	01473990	40°01'50"	75°11'54"	61	2,430	40.4	11.6	41.9	27.0	Urban
11	East Branch Brandywine Creek near Dorlan, Pa.	01480665	40°03'08"	75°43'28"	31.7	291	46.1	51.9	1.1	2.8	Agricultural
12	Stony Creek at Steriger Street at Norristown, Pa.	01473470	40°07'38"	75°20'43"	20.3	1,835	31.0	29.6	36.7	23.7	Urban
13	Pennypack Creek at Paper Mill, Pa.	01467040	40°08'24"	75°04'28"	23.5	3,308	23.2	4.6	63.2	40.6	Urban
14	French Creek near Phoenixville, Pa.	01472157	40°09'05"	75°36'06"	58.9	159	63.1	34.5	1.0	2.5	Agricultural
15	Pigeon Creek at Parker Ford, Pa.	01472100	40°11'48"	75°35'13"	14	393	50.6	45.8	3.3	3.6	Agricultural
16	Delaware River at Trenton, N.J.	01463500	40°13'18"	74°46'42"	6,773	203	74.7	16.5	3.3	6.2	Integrator
17	Little Neshaminy Creek at Valley Road near Neshaminy, Pa.	01464907	40°13'45"	75°07'12"	27	989	35.6	32.0	25.7	17.9	Urban
18	Hay Creek near Birdsboro, Pa.	01471668	40°15'04"	75°48'50"	21	128	76.3	20.6	.4	3.3	Low-intensity agricultural
19	Shabakunk Creek near Lawrenceville, N.J.	01463810	40°15'19"	74°44'17"	11.7	2,774	15.8	14.0	61.9	38.5	Urban
20	Manatawny Creek near Pottstown, Pa.	01471980	40°16'22"	75°40'49"	85.5	226	55.9	41.0	1.6	3.1	Agricultural
21	Pine Run at Chalfont, Pa.	01464710	40°17'20"	75°12'11"	11.8	684	37.4	48.8	12.1	9.8	Mixed
22	Wyomissing Creek at West Reading, Pa.	01471520	40°19'41"	75°56'41"	16	1,964	43.4	24.8	31.1	21.2	Urban
23	Pidcock Creek near New Hope, Pa.	01462100	40°19'46"	74°56'14"	12.7	199	60.8	36.9	.3	1.9	Agricultural
24	Tulpehocken Creek near Bernville, Pa.	01470779	40°24'48"	76°10'19"	70	282	13.1	82.3	3.6	4.4	Agricultural
25	Little Lehigh Creek near East Texas, Pa.	01451425	40°32'34"	75°33'47"	51	384	23.4	68.0	7.5	6.8	Agricultural

**Table 1.** Sites where fish filets, streamwater column, and bed-sediment samples were collected in the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001—Continued

Map locator number (fig. 1)	Site name	U.S. Geological Survey identification number	Latitude	Longitude	Drainage area (square miles)	People per square mile <sup>1</sup>	Land-use characteristics				
							Percent forest <sup>2</sup>	Percent agriculture <sup>2</sup>	Percent urban <sup>2</sup>	Percent impervious surface <sup>2</sup>	Land-use designation
26	Jordan Creek near Schnecksville, Pa.	01451800	40°39'42"	75°37'38"	52	156	32.9	65.6	0.8	2.3	Agricultural
27	Lehigh River at Glendon, Pa.	01454700	40°40'09"	75°14'12"	1,356	442	63.0	23.3	6.7	8.6	Integrator
28	Brodhead Creek at Stroudsburg, Pa.	01442500	40°59'14"	75°11'02"	256	273	83.3	7.4	4.5	5.7	Forested
29	Bush Kill Creek at Bushkill, Pa.	01439500	41°05'17"	75°00'42"	126	57	86.6	.6	1.0	4.2	Forested
30	Flat Brook near Flatbrookville, N.J.	01440000	41°06'24"	74°57'09"	65	38	88.0	7.0	.7	2.9	Forested
31	Delaware River at Port Jervis, N.Y.	01434000	41°22'14"	74°41'52"	3,076	48	84.3	10.6	1.0	4.6	Integrator
32	Neversink River near Godeffroy, N.Y.	01437500	41°26'28"	74°36'08"	305	87	89.2	3.0	3.0	6.3	Forested
33	Lackawaxen River at Hawley, Pa.	01431500	41°28'34"	75°10'21"	288	84	74.6	18.8	.9	4.9	Low-intensity agricultural
34	Neversink River near Claryville, N.Y.	01435000	41°53'24"	74°35'25"	69	9	99.3	.5	.1	1.7	Forested
35	W.Br. Delaware River at Walton, N.Y.	01423000	42°09'58"	75°08'25"	331	45	75.4	23.1	.9	2.3	Low-intensity agricultural

<sup>1</sup> U.S. Department of Commerce, 1990.

<sup>2</sup> Fischer, 1999.

Fish were collected using a direct current electrofishing backpack. A top predator species, usually smallmouth bass (*Micropterus dolomieu*), was targeted for collection. Chain pickerel (*Esox niger*), resident brown trout (*Salmo trutta*), largemouth bass (*Micropterus salmoides*), or rock bass (*Ambloplites rupestris*) were collected from sampling reaches lacking smallmouth bass. One to three specimens were collected at each site. Two- to three-year-old fish were needed for this study (Krabbenhoft and others, 1999). Age was estimated by size class during collection. In 1999, specimens were measured for total length (mm), weighed (g), placed in sealable plastic bags, put on dry ice, and shipped to the USGS Wisconsin Mercury Research Laboratory (WMRL) in Middleton, Wis., for analysis (Krabbenhoft and others, 1999). In 2000, specimens were measured for total length, weighed, filleted in the field, put on dry ice, and shipped to the WMRL for analysis. The fish were filleted in the field to avoid thawing of the fish and refreezing. In 2001, the same field procedures used in 2000 were followed, and samples were sent to the USGS National Water Quality Laboratory (NWQL) for analysis.

Streamwater samples for tHg and MeHg were collected using the trace-metal clean methods of Fitzgerald and Watras (1989). Personnel collecting the samples wore arm-length latex gloves. The persons doing the processing wore latex gloves and used the "clean-hands, dirty-hands" technique of Olsen and DeWild (1999). Samples were placed in teflon containers that had been hot acid cleaned, partially filled with 1 percent hydrochloric acid for storage purposes, and double bagged in sealable plastic bags (Krabbenhoft and others, 1999). The tHg samples were acidified to 1 percent hydrochloric acid by volume, and the MeHg samples were placed in a dark cooler until they could be frozen (Krabbenhoft and others, 1999) and shipped to the WMRL.

Bed-sediment samples were collected using the trace-element sampling protocols from the NAWQA Program (Shelton and Capel, 1994). Personnel wearing latex gloves used a polypropylene scoop to sample the surficial layer (estimated at 2-3 cm deep), which is assumed to be recently deposited sediment in the stream, from random locations within the designated sampling area. Approximately 50 scoops were placed in a bowl that had been cleaned in accordance with the trace-element sampling protocols. After the material was mixed thoroughly, an aliquot was removed, placed

in a teflon vial, frozen, and sent to the WMRL for analysis of tHg, MeHg, and Loss-On-Ignition (LOI), a surrogate for organic carbon.

### **Fish, Streamwater, and Bed-Sediment Laboratory Analysis Procedures**

Fish-fillet samples were placed into acid-washed borosilicate glass jars and freeze-dried. The dry product was homogenized and digested in a sealed teflon pressure vessel with microwave heating and the addition of nitric and hydrochloric acid, followed by hydrogen peroxide. Cold-vapor atomic absorption spectrophotometry with flow injection sample introduction and stannous chloride reduction was used to determine the concentration of tHg in the sample. A full description of laboratory procedures can be found in Brumbaugh and others (2001).

The NWQL and WMRL used different USEPA methods (method 3052 and method 1631, respectively) for determination of tHg (J.R. Garbarino, U.S Geological Survey, written commun., 2003). The primary difference that could affect comparability of results is a higher detection limit for the WMRL method (0.02 µg/g wet weight) (Brumbaugh and others, 2001) than for the NWQL method (0.001 µg/g dry weight) (J.R. Garbarino, U.S Geological Survey, written commun., 2003). This should not affect the results for the Delaware River Basin study because all sample concentrations were orders of magnitude higher than the method detection limit of either testing method.

Streamwater samples were analyzed for tHg concentration using cold-vapor atomic-fluorescence spectroscopy (CVAFS) (Olson and DeWild, 1999; Olson and others, 1997) at the WMRL. Water samples also were analyzed for MeHg concentration with the distillation and aqueous phase ethylation method of Horvat and others (1993) and with CVAFS. Method reporting limits (MRL) for concentrations of tHg and MeHg in water were 0.04 and 0.025 ng/L, respectively (Olsen and DeWild, 1999).

Bed-sediment samples were analyzed for concentrations of tHg using the CVAFS technique at the WMRL. These samples were predigested with nitric and sulfuric acids in a sealed teflon pressure vessel at 125°C for a minimum of 2 hours. The cooled sample was then diluted with a 5-percent bromochloride solution and oxidized at 50°C for a minimum of 12 hours (Krabbenhoft and others, 1999). The distillation and aqueous phase ethy-

lation method of Horvat and others (1993) and CVAFS (Krabbenhoft and others, 1999) were used to determine MeHg concentrations. The MRLs for tHg and MeHg in bed sediments were 0.04 and 0.025 ng/g, respectively (Olsen and DeWild, 1999).

### **Quality Control**

Several types of quality-control samples were analyzed to assure a sound data set. No quality-control samples were done for fish other than the laboratory's own quality control. No extra fish were taken as a replicate sample. In 1998, a split bed-sediment tHg sample was analyzed at the WMRL. In 1999, another split bed-sediment tHg sample was analyzed at the WMRL. An additional streamwater-column sample was analyzed for tHg and MeHg in 1999.

### **Data Analysis**

Concentrations below the MRLs were set to one-half the reporting limit for statistical and graphical analysis. This technique has been used in reports by Bilger and others (1999) and by Stahl and Sobat (2000). Land-use and population factors were generated for each site. Methylation efficiencies (MeHg/tHg) of sediment and water samples were calculated according to Krabbenhoft and others (1999) and Brumbaugh and others (2001). For comparisons among land-use classes, sites were defined as follows: forested basins have greater than 80 percent forest, low intensity-agricultural basins have from 15 to 25 percent agricultural land and more than 65 percent forested land, agricultural basins have greater than 25 percent agriculture and less than 8 percent impervious surface, urban basins have 15 percent or greater impervious surface, and mixed basins have between 8 and 14 percent impervious surface and less than 80 percent forested land from 1992 satellite derived MAPPER land-use data (McMahon and Cuffney, 2000). In addition, several large watersheds (drainage area greater than 800 mi<sup>2</sup>) with multiple land uses were classified as 'integrator sites.'

Prior to data analysis, a Pearson correlation was run on the environmental data. This was done to reduce the multicollinearity within the data set. The correlated variable with fewer data points or that was less normally distributed was removed from the data set. The remaining variables were analyzed using statistical and graphical approaches.

Fish-fillet data used for all statistical (and most graphical) analyses were limited to smallmouth bass. Limiting certain analyses to the largest single-species data set avoided the problem of interspecies differences in metabolism and in Hg accumulation rates (Goldstein and others, 1996; Brumbaugh and others, 2001). For sites having specimens ranging widely in size, the laboratory separated specimens into two separate batches prior to analysis. In these cases, only the sample with the larger mean length was retained for inclusion in this report. Dry-weight concentrations were converted to wet-weight concentrations by using percent moisture as the divisor, or, where percent moisture was not available, an estimate of 80 percent moisture was used. Hg concentrations in smallmouth bass fillets were normalized to mean sample total length prior to statistical and graphical analyses. Total length is related to age of fish, which has been shown in other studies to influence Hg concentrations. Concentration of tHg in bed sediment was normalized to LOI.

## **DISTRIBUTION AND CONCENTRATIONS OF TOTAL MERCURY AND METHYLMERCURY**

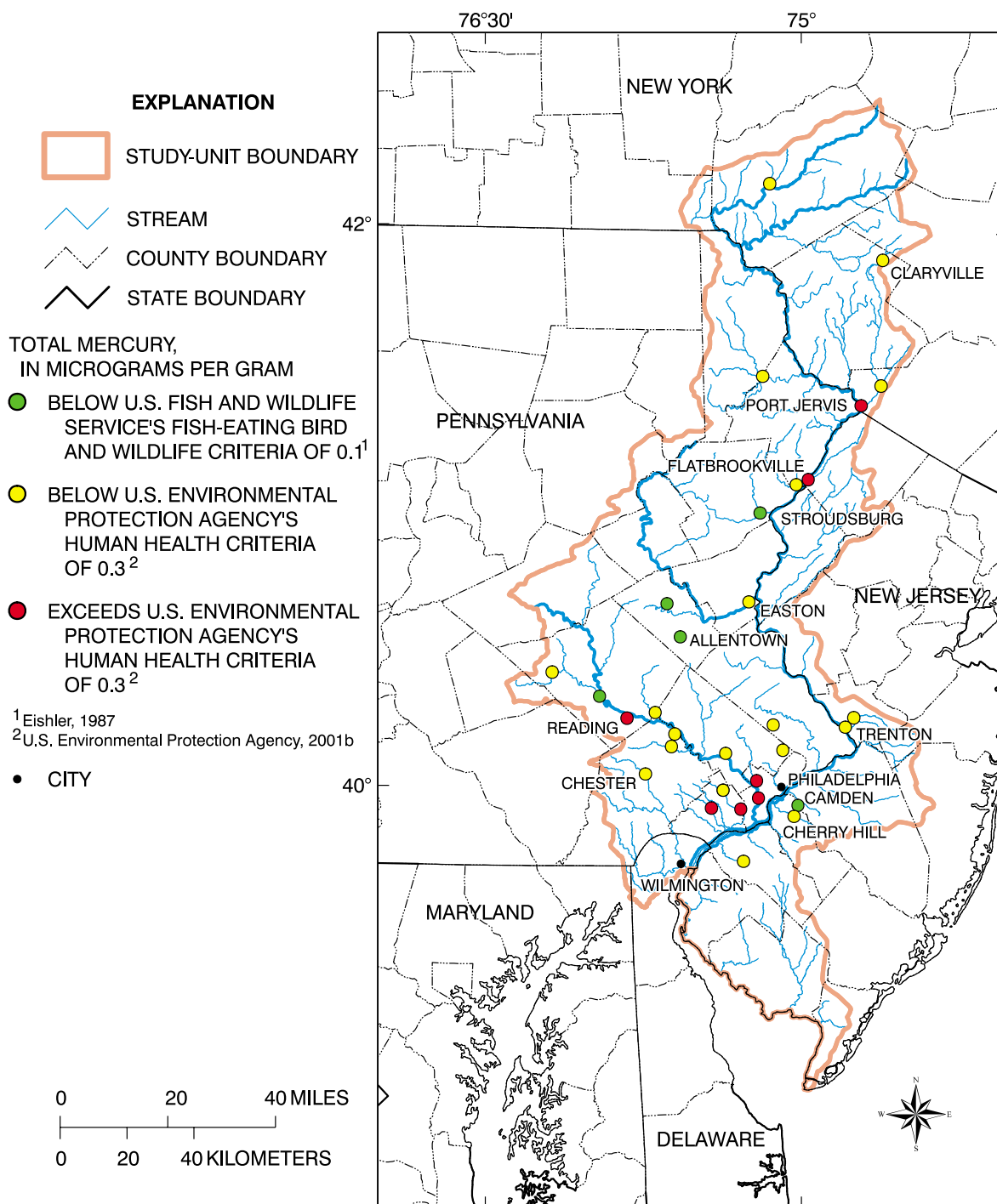
Fish tissue, water, and bed-sediment samples were obtained from streams throughout the Delaware River Basin. The West Branch Delaware River at Walton, N.Y., was the northernmost site. Raccoon Creek near Swedesboro, N.J., was the southernmost site.

Concentrations of Hg were detectable in all fish-tissue samples. Concentrations of tHg were detected in all streamwater and bed-sediment samples. Samples from 19 of the 24 water-collection sites had detectable concentrations of MeHg. Of the 28 bed-sediment collection sites, all had detectable concentrations of MeHg.

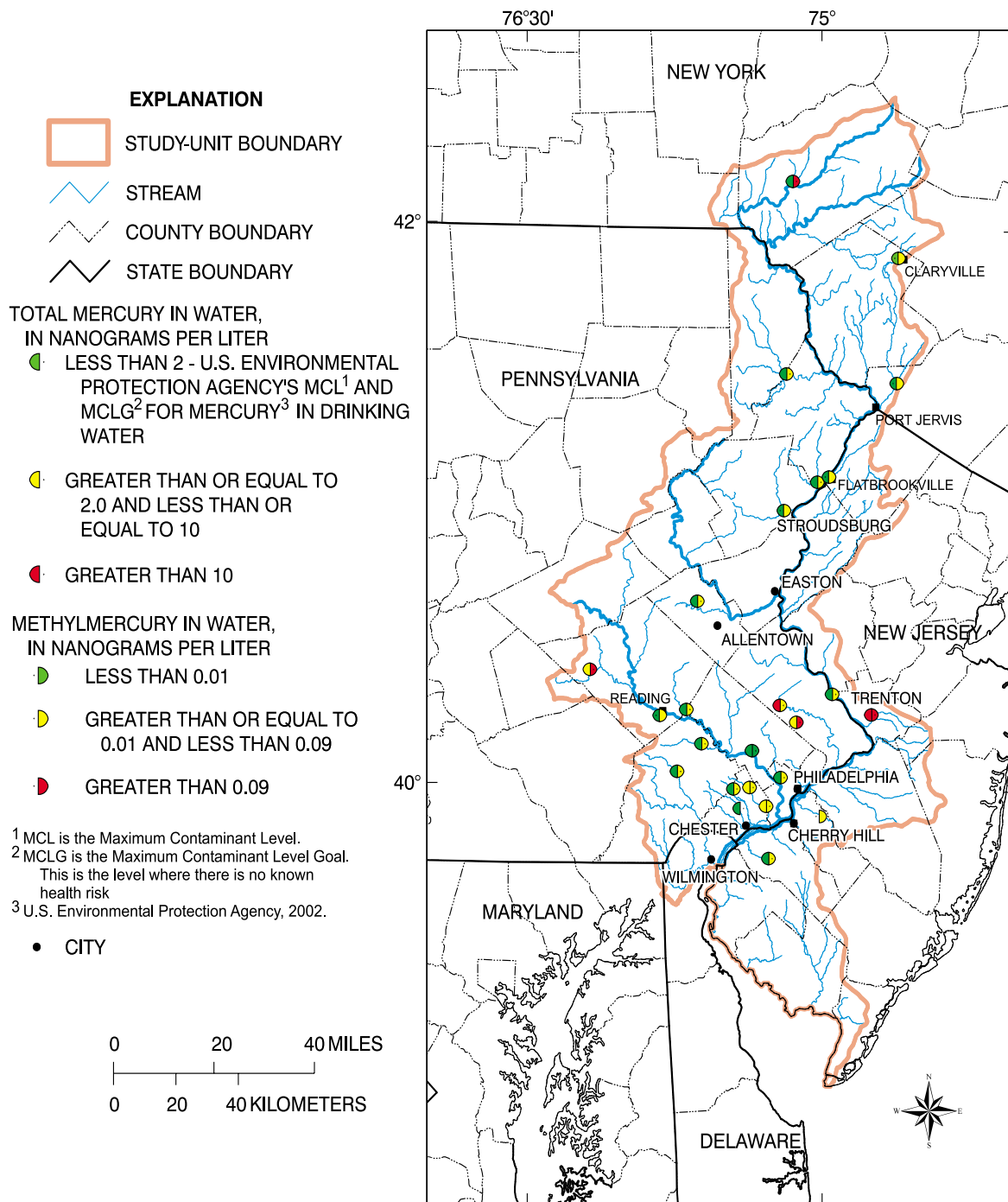
### **Patterns of Distribution**

The distribution of Hg was highly variable throughout the basin (figs. 2, 3, and 4). Fish-tissue concentrations that exceeded human health and wildlife criteria were found in the urbanized south and the forested north (fig. 2). A north-south plot of tHg concentrations in smallmouth bass (fig. 5) indicates a pattern of higher length-normalized tHg concentrations in the southern section, an area of higher population density and industrialization, and in the northern section, an area of relatively low population density. The lowest concentrations tended to be at sites in the middle section of the study area.

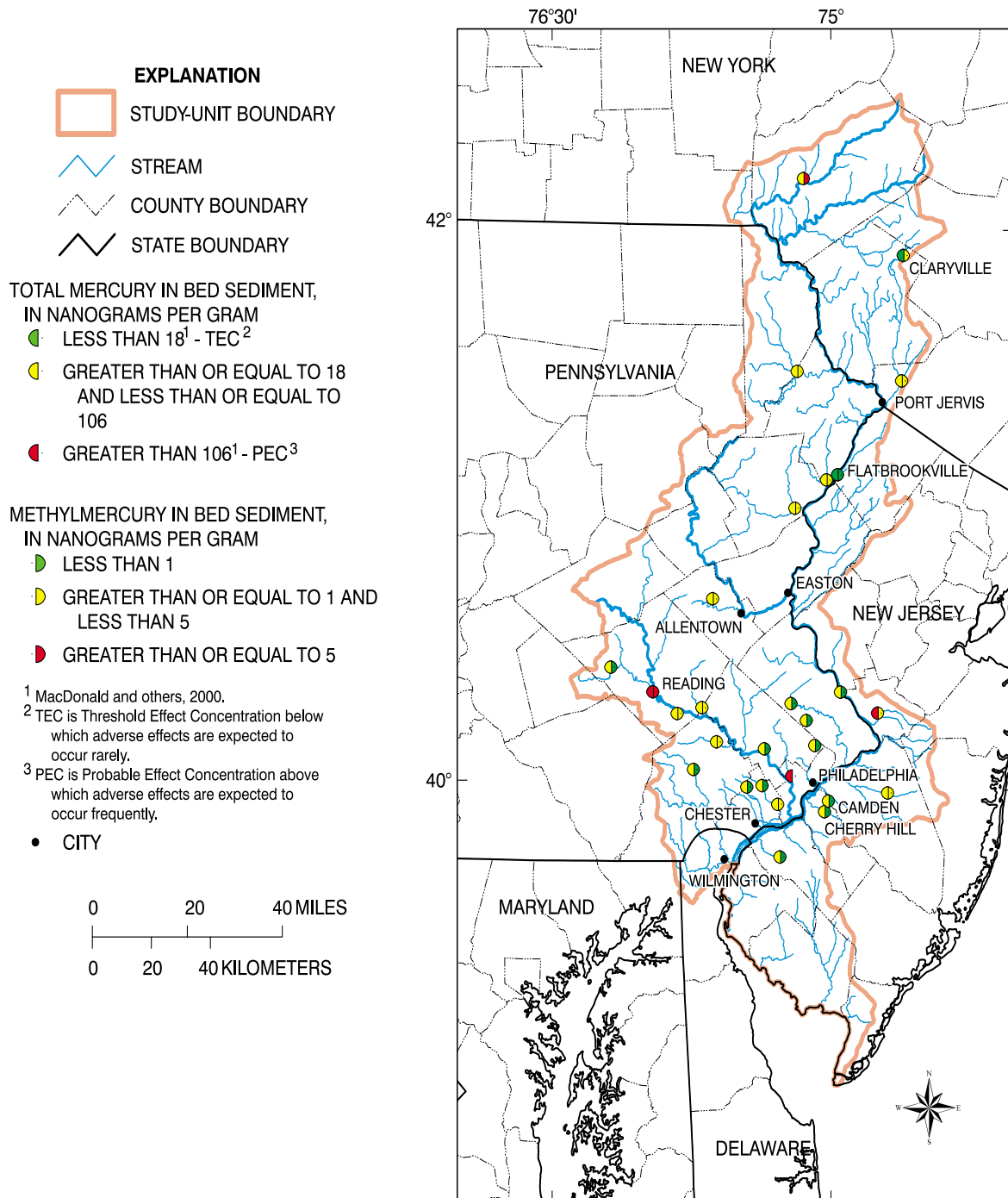




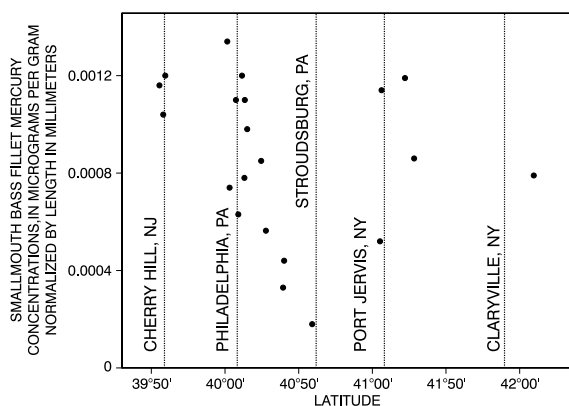
**Figure 2.** Distribution of mercury concentrations in fish fillets within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 3.** Distribution of mercury and methylmercury concentrations in streamwater within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 4.** Distribution of mercury and methylmercury concentrations in bed sediment within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 5.** Relation between mercury concentrations in smallmouth bass fillets (normalized by total length) and latitude within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001. (Locations of towns and cities referred to are shown on figure 2.)

Concentrations of tHg in the majority of the water samples were below the USEPA Maximum Contaminant Level (MCL) of 2 ng/L tHg in drinking water (U.S. Environmental Protection Agency, 2002). Only six sites were above this MCL, and these were in the more highly urbanized area of the basin (fig. 3). However, the sites with higher concentrations of MeHg were in the more urbanized (southern) and the more forested (northern) areas of the basin. This pattern is similar to that observed with the fish-tissue Hg patterns.

The distribution of Hg in bed-sediment samples was similar to that observed in the streamwater samples. The two sites under the Threshold Effect Concentration (TEC) of 18 ng/g tHg (MacDonald and others, 2000) were in the northern section of the Delaware River Basin (fig. 4). The three highest tHg concentrations were observed at sites in the more populated area of the basin. A northern, forested site and a middle, urban site had the two highest MeHg concentrations in the basin. The urbanized southern sites had the lowest MeHg concentrations.

## Concentrations

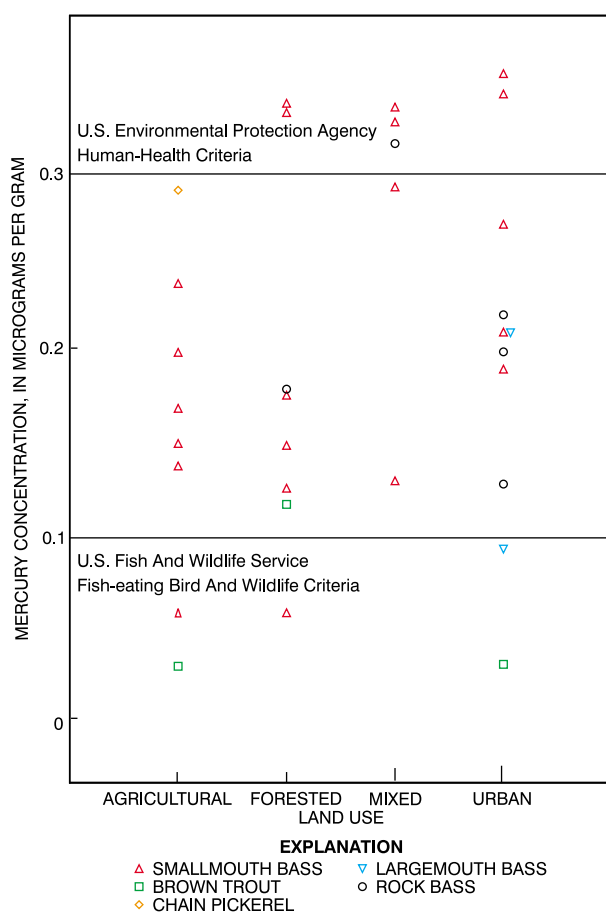
Fish-tissue tHg concentrations ranged from 0.03 to 0.35  $\mu\text{g/g}$  wet weight (Appendix). The internal quality-control tests performed at the WMRL for fish tissue indicated good accuracy and precision except when sample concentrations were very low (Brumbaugh and others, 2001). Method blanks were near or below the instrument detection limit for eight of the nine test blanks, resulting in a higher MRL of 0.020  $\mu\text{g/g}$  wet weight (Brumbaugh and others, 2001).

Streamwater tHg sample concentrations ranged from 0.43 to 22 ng/L (Appendix) and MeHg concentrations ranged from less than the MRL to 0.28 ng/L. The split sample for tHg in water from the 1999 survey (Flat Brook near Flatbrookville, N.J.) showed a 175-percent difference in results, with a sample tHg concentration of 1.79 ng/L and a split tHg concentration of 0.65 ng/L. The MeHg split sample from the same site showed a 250-percent error, with a sample MeHg concentration of 0.049 ng/L and a split sample MeHg concentration of 0.014 ng/L. The NMPP reported differences between split samples to be less than 50 percent at higher tHg and MeHg concentrations and differences greater than 100 percent for lower tHg and MeHg concentrations (Brumbaugh and others, 2001).

Bed-sediment sample tHg concentrations ranged from 1.5 to 380 ng/g (Appendix) and MeHg concentrations ranged 0.01 to 8.7 ng/g. The bed-sediment quality-control split samples showed better results than the streamwater samples. Split sample tHg concentrations showed a 40 and 43 percent difference between the first and second samples. The Little Neshaminy sample had concentrations of 40.1 and 66.9 ng/g (40 percent), and the French Creek sample had concentrations of 77.7 and 54.3 ng/g for a difference of 43 percent. No MeHg split samples were collected for bed sediments.

## Human-Health and Wildlife Criteria

Fish-fillet tHg data were compared to human-health and wildlife criteria to assess potential effects in the Delaware River Basin. Concentrations of tHg in fish fillets exceeded the USEPA human-health criteria of 0.3 µg/g wet-weight fillets (U.S. Environmental Protection Agency, 2001b) in 7 of the 32 samples (22 percent) from 31 sites (fig. 6, table 2). Of the seven samples that exceeded the USEPA human-health criteria, four were from streams near Philadelphia, Pa., one was from near Reading, Pa., and the other two were from the Pocono area in New York and New Jersey.



**Figure 6.** Mercury concentrations in fish fillets, U.S. Environmental Protection Agency human-health criteria (U.S. Environmental Protection Agency, 2001b), and U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria (Eisler, 1987) compared with land-use categories (Fischer, 1999) within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

The U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria of 0.1 µg/g wet weight in whole fish (Eisler, 1987) was exceeded in 27 of the 32 fillet samples (84 percent) from the 31 sites where fish were collected. The criteria were set using whole fish; thus, a direct comparison to the criteria is not entirely valid, although most of the Hg in fish typically is in muscle (Wachs, 1985; Goldstein and others, 1996). Fillet samples just over the criteria limit may actually be below the criteria level if whole fish had been analyzed. A direct relation between fillet concentrations and whole-fish concentrations has been described by Goldstein and others (1996) and could be used to extrapolate fish-eating bird and wildlife criteria, but these regressions must be species-adjusted (Goldstein and others, 1996).

## Factors Affecting Concentrations

Hg concentrations in fish fillets, water, and bed sediment have different distribution patterns along the length of the Delaware River Basin. Patterns tend to coincide with land use. The northern section of the basin is mostly forested, and the southern section is mostly urban; the area in-between has mixed land uses. Within each land-use category, different factors influence the concentrations of Hg in fish fillets, water, and bed sediment.

**Table 2.** A summary of mercury concentrations in fish filets and exceedances of the U.S. Environmental Protection Agency human-health criteria, and the U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria from selected sites in the Delaware River Basin, 1998 through 2001

[USEPA, U.S. Environmental Protection Agency; USFWS, U.S. Fish and Wildlife Service; µg/g, micrograms per gram]

Map locator number (fig. 1)	Site name	Fish species	Number of fish in sample	Mercury concentration (µg/g)	Exceed USEPA's human-health criteria? <sup>1</sup> (fillet) (0.3 µg/g)	Exceed USFWS fish-eating bird and wildlife criteria? <sup>2</sup> (whole fish) (0.1 µg/g)
1	Raccoon Creek near Swedesboro, N.J.	Chain Pickerel	1	0.29	No	Yes
2	Cooper River at Haddonfield, N.J.	Largemouth bass	3	.21	No	Yes
3	Darby Creek near Darby, Pa.	Smallmouth bass	2	.35	Yes	Yes
4	Ridley Creek near Media, Pa.	Rock bass	3	.31	Yes	Yes
5	South Branch Pennsauken Creek at Cherry Hill, N.J.	Largemouth bass	4	.09	No	No
6	Schuylkill River at Philadelphia, Pa.	Smallmouth bass	5	.32	Yes	Yes
9	Darby Creek at Foxcroft, Pa.	Smallmouth bass	1	.19	No	Yes
		Rock bass	2	.22	No	Yes
10	Wissahickon Creek below Walnut Lake near Manayunk, Pa.	Smallmouth bass	1	.34	Yes	Yes
11	East Branch Brandywine Creek near Dorlan, Pa.	Smallmouth bass	2	.14	No	Yes
12	Stony Creek at Steriger Street at Norristown, Pa.	Smallmouth bass	3	.21	No	Yes
13	Pennypack Creek at Paper Mill, Pa.	Rock bass	3	.13	No	Yes
14	French Creek near Phoenixville, Pa.	Smallmouth bass	3	.20	No	Yes
15	Pigeon Creek at Parker Ford, Pa.	Smallmouth bass	1	.15	No	Yes
16	Delaware River at Trenton, N.J.	Smallmouth bass	5	.29	No	Yes
17	Little Neshaminy Creek at Valley Road near Neshaminy, Pa.	Smallmouth bass	2	.27	No	Yes
18	Hay Creek near Birdsboro, Pa.	Smallmouth bass	1	.33	Yes	Yes
19	Shabakunk Creek near Lawrenceville, N.J.	Rock bass	2	.20	No	Yes
20	Manatawny Creek near Pottstown, Pa.	Smallmouth bass	3	.17	No	Yes
22	Wyomissing Creek at West Reading, Pa.	Brown trout	2	.03	No	No
24	Tulpehocken Creek near Bernville, Pa.	Smallmouth bass	1	.24	No	Yes
25	Little Lehigh Creek near East Texas, Pa.	Brown trout	3	.03	No	No
26	Jordan Creek near Schnecksville, Pa.	Smallmouth bass	3	.06	No	No
27	Lehigh River at Glendon, Pa.	Smallmouth bass	5	.13	No	Yes
28	Brodhead Creek at Stroudsburg, Pa.	Smallmouth bass	2	.06	No	No
29	Bush Kill Creek at Bushkill, Pa.	Smallmouth bass	2	.13	No	Yes
30	Flat Brook near Flatbrookville, N.J.	Smallmouth bass	2	.33	Yes	Yes
31	Delaware River at Port Jervis, N.Y.	Smallmouth bass	4	.33	Yes	Yes
32	Neversink River near Godeffroy, N.Y.	Rock bass	2	.18	No	Yes
33	Lackawaxen River at Hawley, Pa.	Smallmouth bass	2	.18	No	Yes
34	Neversink River near Claryville, N.Y.	Brown trout	2	.12	No	Yes
35	West Branch Delaware River at Walton, N.Y.	Smallmouth bass	2	.15	No	Yes

<sup>1</sup> U.S. Environmental Protection Agency human-health criteria (U.S. Environmental Protection Agency, 2001b).

<sup>2</sup> U.S. Fish and Wildlife Service fish-eating bird and wildlife criteria (Eisler, 1987).

## Fish fillets

On a basinwide scale, length-normalized tHg concentrations in smallmouth bass fillets were not strongly correlated with any land-use or landscape factor (table 3). The only significant correlation (at  $p < 0.05$ ) was with percent impervious land surface. There was a weak correlation with LOI-normalized tHg concentrations in bed sediments (fig. 8). However, this relation was strongly influenced by a few data points at the low and high ends of the range. Length-normalized tHg concentrations in smallmouth bass fillets vary greatly among the sparsely populated, northern basins and generally increase with population density in the middle and southern parts of the basin. Concentrations of tHg in fish fillets tend to be highest in the more densely populated areas where concentrations of tHg in bed sediments are relatively high (fig. 7).

Thus, when the sparsely populated (<100 people per square mile), northern-region sites are excluded from the analysis, effects of urbanization are observed (table 3). Among sites in watersheds inhabited by 100 or more people per square mile, length-normalized tHg concentrations in smallmouth bass fillets were positively correlated with population density, percent urban land cover, LOI-normalized tHg concentrations in bed sediment, and impervious land surface. Concentrations of tHg (length-normalized) in fillets from sites in this group were negatively correlated with latitude, percent wetland, percent septic, and methylation efficiency in bed sediment; a weak negative correlation is observed with elevation. Concentrations of tHg in smallmouth bass fillets were not significantly correlated with MeHg concentrations in water or in bed sediments, either on a basinwide scale or after removal of the sparsely

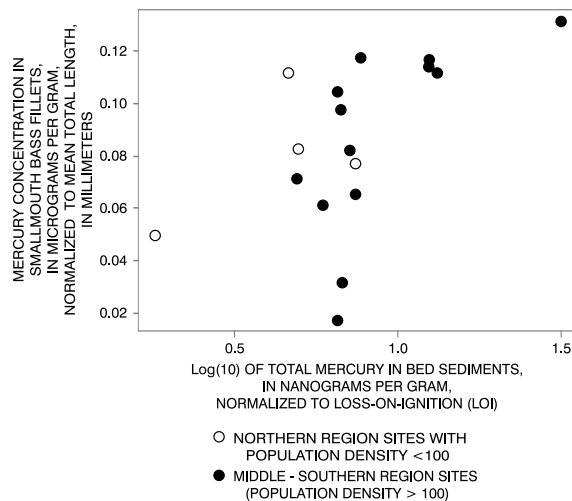
**Table 3.** Results of Spearman rank correlation analysis between mercury concentration in smallmouth bass (*Micropterus dolomieu*) fillets and environmental and landscape variables for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

[\*\*,  $p \leq 0.01$ ; \*,  $p = 0.05$ ; ns, not significant ( $p > 0.05$ ); LOI, Loss-On-Ignition;  $\geq$ , greater than or equal to;  $<$ , less than; numbers of observations are shown in parentheses]

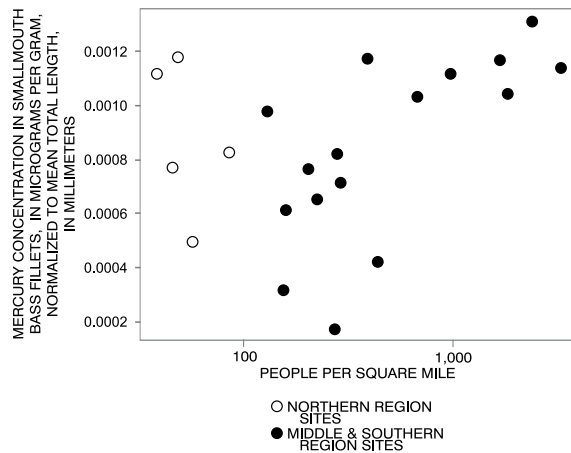
Environmental and landscape variables	Smallmouth bass fillets Total mercury/mean sample total length		
	All sites	Sites in basins with $\geq 100$ people per square mile	Sites in basins with <100 people per square mile
Estimated population density for 1997 <sup>1</sup>	ns (21)	0.69** (16)	ns (5)
Forested land cover (percent of total area) <sup>2</sup>	ns (21)	ns (16)	ns (5)
Agricultural land cover (percent of total area) <sup>2</sup>	ns (21)	ns (16)	ns (5)
Urban land cover (percent of total area) <sup>2</sup>	ns (21)	.61* (16)	ns (5)
Impervious land surface (percent of total area) <sup>2</sup>	0.47* (21)	.65** (16)	ns (5)
Wetland land cover (percent of total area) <sup>2</sup>	ns (21)	-.66** (16)	ns (5)
Septic density <sup>1</sup>	ns (21)	ns (16)	ns (5)
Septic percent (percent of population) <sup>1</sup>	ns (21)	-.56** (16)	ns (5)
Elevation	ns (21)	-.52* (16)	ns (5)
Latitude	ns (21)	-.70** (16)	ns (5)
Methylmercury in water	ns (16)	ns (13)	ns (5)
Methylmercury in bed sediments	ns (16)	ns (13)	ns (5)
Total mercury in water	ns (16)	ns (13)	ns (5)
Total mercury/ LOI in bed sediments	.55* (17)	.71** (13)	ns (5)
Methylation efficiency in water	ns (16)	ns (13)	ns (5)
Methylation efficiency in bed sediments	ns (16)	-.64* (12)	ns (5)
Sulfate in water	ns (21)	ns (16)	ns (5)
Dissolved organic carbon in water	ns (21)	ns (16)	ns (5)
pH	ns (21)	ns (16)	ns (5)

<sup>1</sup> U.S. Department of Commerce, 1990.

<sup>2</sup> U.S. Geological Survey, 1992.



**Figure 7.** Relation between total mercury concentrations in smallmouth bass fillets (normalized by total length) and total mercury concentrations in bed sediment (normalized by LOI) within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001. [ $<$ , less than;  $\geq$  greater than or equal to]



**Figure 8.** Relation between total mercury concentrations in smallmouth bass fillets (normalized by total length) and estimated population density (1997) (U.S. Department of Commerce, 1990) within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

populated northern sites (table 3). No significant and reasonably strong correlations were observed when a separate analysis was conducted on the small group of northern-region sites with less than 100 people per square mile (table 3).

### Streamwater

Streamwater-sample tHg concentrations were correlated with urban indicators, when viewed on a basin-wide scale. Concentrations of tHg were positively correlated with population density, impervious land surface, and urban land cover (table 4, fig. 9). There was a weak, positive correlation with sulfate concentrations in the water column. Concentrations of tHg were negatively correlated with forested land cover. There appears to be an upward trend in tHg as areas become more populated in the basin, even with the large error range on actual concentration values. There is also a weak positive correlation with dissolved organic carbon (DOC) at  $p < 0.05$  (table 4).

Streamwater MeHg concentrations were not strongly correlated with any landscape or environmental variable (table 4, fig. 10). However, methylation efficiency of streamwater was negatively correlated with population density, impervious land surface, and urban land cover (table 4, fig. 11). This is the inverse of the correlation observed with tHg and population variables. The rate of change from tHg to MeHg appears to be higher in the more forested areas of the basin than the less forested areas.

### Bed sediment

Bed-sediment tHg concentrations also were correlated with urban indicators similar to the results seen for tHg in streamwater. The positive correlations were with population density, impervious land surface, and urban land cover. The negative correlations were with forested land cover, latitude, and elevation (table 5, fig. 12). The tHg concentrations showed a positive relation with sulfate concentrations in the water column, similar to the water and sulfate interaction (table 5).



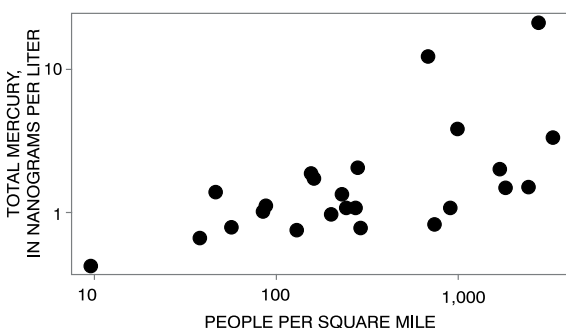
**Table 4.** Results of Spearman rank correlation analyses between environmental and landscape variables and mercury in streamwater samples for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

[LOI, Loss-On-Ignition; \*\*\*,  $p \leq 0.001$ ; \*\*,  $p \leq 0.01$ ; \*,  $p = 0.05$ ; ns, not significant ( $p > 0.05$ ); —, same variable. Number of observations are shown in parentheses.]

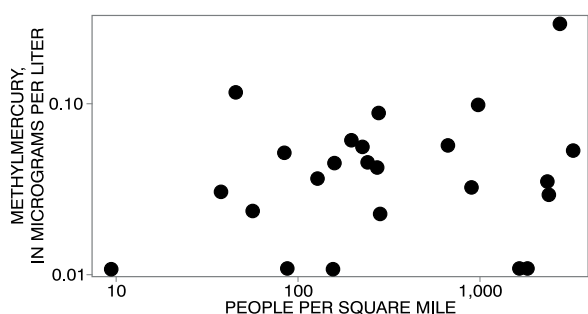
Environmental and landscape variables	Streamwater column		
	Total mercury	Methylmercury	Methylation efficiency
Estimated population density 1997 <sup>1</sup>	0.63*** (24)	ns (24)	-0.54** (23)
Forested land cover (percent of total area) <sup>2</sup>	-.69*** (24)	ns (24)	ns (23)
Agricultural land cover (percent of total area) <sup>2</sup>	ns (24)	ns (24)	ns (23)
Urban land cover (percent of total area) <sup>2</sup>	.67*** (24)	ns (24)	-.59** (23)
Impervious land surface (percent of total area) <sup>2</sup>	.57** (24)	ns (24)	-.53** (23)
Wetland land cover (percent of total area) <sup>2</sup>	ns (24)	ns (24)	ns (23)
Septic density <sup>1</sup>	ns (24)	ns (24)	ns (23)
Elevation	ns (24)	ns (24)	ns (23)
Latitude	ns (24)	ns (24)	ns (23)
Methylmercury in water	ns (23)	—	ns (23)
Methylmercury in bed sediments	ns (23)	ns (24)	ns (23)
Total mercury in water	—	ns (24)	-.62** (23)
Total mercury in bed sediments	.65*** (24)	ns (24)	ns (23)
Total mercury/ LOI in bed sediments	.63*** (24)	ns (24)	ns (23)
Methylation efficiency in water	-.60** (23)	ns (23)	—
Methylation efficiency in bed sediments	ns (23)	ns (24)	ns (23)
Sulfate in water	.46* (24)	ns (24)	ns (23)
Dissolved organic carbon in water	.41* (24)	ns (24)	ns (23)
pH	ns (24)	ns (24)	ns (23)

<sup>1</sup> U.S. Department of Commerce, 1990.

<sup>2</sup> U.S. Geological Survey, 1992.



**Figure 9.** Relation between population density and total mercury concentrations in streamwater samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

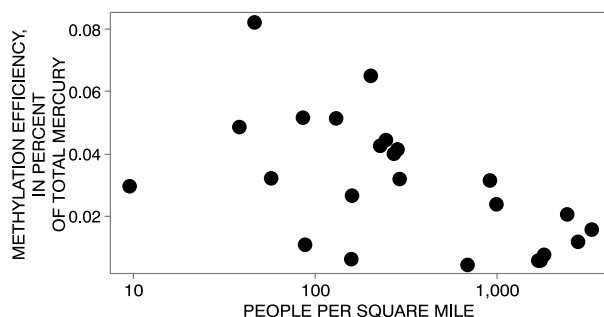


**Figure 10.** Relation between population density and methylmercury concentrations in streamwater samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

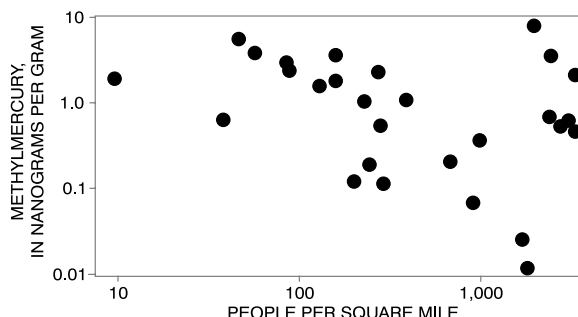
As in the water column, MeHg was not strongly correlated with any landscape or environmental variable (table 5, fig. 13). A slight decline with an increase in population density can be observed in figure 13 until the population density becomes greater than 1,000 people per square mile. A threshold response can be observed between MeHg concentrations in bed sediment and percent wetland (fig. 14). None of the higher-percentage wetland sites have low MeHg concentrations.

Methylation efficiency in bed sediment was negatively correlated with population density, impervious land surface, agricultural land cover and urban land cover (table 5), similar to what was

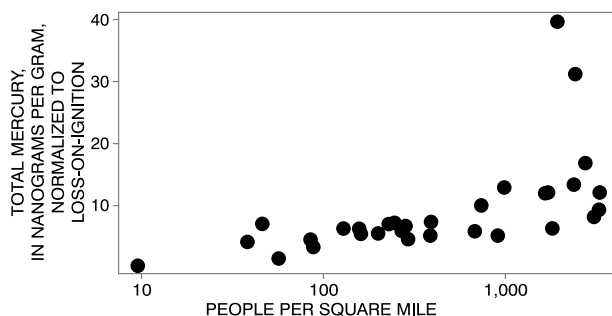
observed in the water-column interactions. Positive correlations included forested land cover, elevation, and latitude. This is the inverse of the correlations for tHg in bed sediment and is similar to the results observed for streamwater tHg and MeHg concentrations. Methylation efficiency in bed sediment is an upside-down, bell-shaped curve with methylation efficiencies being higher in the least populated sites and the most populated sites of the Delaware River Basin (fig. 15). This negative correlation between methylation efficiency and population density corresponds with an opposite trend in relation to latitude (table 5).



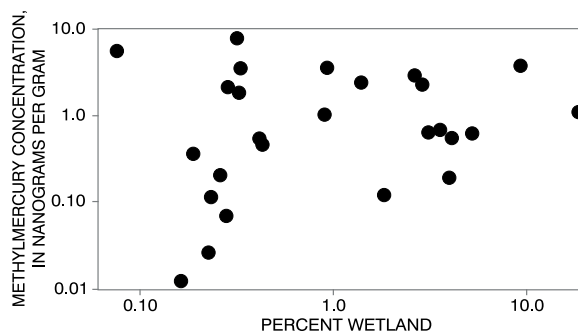
**Figure 11.** Relation between population density and methylation efficiency in streamwater samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 13.** Relation between population density and methylmercury concentrations in bed-sediment samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 12.** Relation between population density and total mercury concentrations in bed-sediment samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.



**Figure 14.** Relation between methylmercury concentrations in bed-sediment samples and wetlands within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

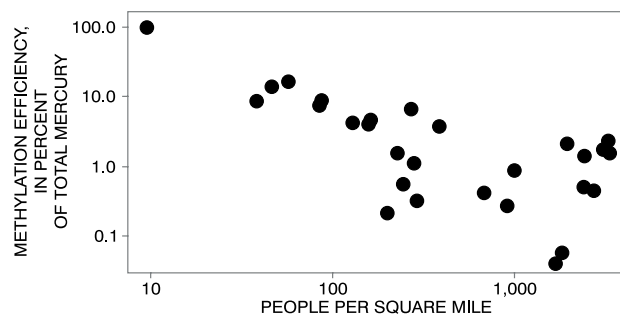
**Table 5.** Results of Spearman rank correlation analyses between environmental and landscape variables and mercury in bed-sediment samples for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

[LOI, Loss-On-Ignition; \*\*\*,  $p \leq 0.001$ ; \*\*,  $p \leq 0.01$ ; \*,  $p = 0.05$ ; ns, not significant ( $p > 0.05$ ); —, same variable;  $\leq$ , less than or equal to;  $>$ , greater than. Numbers of observations are shown in parentheses.]

Environmental and landscape variables	Bed sediment		
	Total mercury/ LOI	Methylmercury	Methylation efficiency
Estimated population density 1997 <sup>1</sup>	0.74*** (30)	ns (28)	-0.62*** (28)
Forested land cover (percent of total area) <sup>2</sup>	-.64*** (30)	0.45* (28)	.63*** (28)
Agricultural land cover (percent of total area) <sup>2</sup>	ns (30)	ns (28)	-.47** (28)
Urban land cover (percent of total area) <sup>2</sup>	.69*** (30)	ns (28)	-.49** (28)
Impervious land surface (percent of total area) <sup>2</sup>	.61*** (30)	ns (28)	-.43* (28)
Wetland land cover (percent of total area) <sup>2</sup>	ns (30)	ns (28)	ns (28)
Septic density <sup>1</sup>	ns (30)	ns (28)	-.55** (28)
Elevation	-.56** (30)	ns (28)	.56** (28)
Latitude	-.48* (30)	.46* (28)	.62*** (28)
Methylmercury in water	ns (24)	ns (24)	ns (24)
Methylmercury in bed sediments	ns (28)	—	.82*** (28)
Total mercury in water	.63*** (24)	-.41* (23)	ns (23)
Total mercury in bed sediments	.67*** (30)	ns (28)	ns (28)
Total mercury/ LOI in bed sediments	—	ns (28)	-.40* (28)
Methylation efficiency in water	ns (23)	ns (23)	ns (23)
Methylation efficiency in bed sediments	-.40* (28)	.84*** (28)	—
Sulfate in water	.64*** (29)	ns (27)	-.52** (27)
Dissolved organic carbon in water	ns (29)	ns (27)	ns (27)
pH	ns (30)	ns (28)	ns (28)

<sup>1</sup> U.S. Department of Commerce, 1990.

<sup>2</sup> U.S. Geological Survey, 1992.



**Figure 15.** Relation between population density and methylation efficiency in bed-sediment samples within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

Methylation efficiency in bed sediment was negatively correlated with water-column sulfate concentrations. This is similar to the negative correlation between methylation efficiency in stream-water and water-column sulfate concentrations. The forested sites in the northern latitudes, plus a mixed land-use site in the Coastal Plain (low-gradient) streams, had the highest methylation efficiencies and the lowest sulfate concentrations. The agricultural, urban, and mixed land-use sites had higher sulfate concentrations and lower bed-sediment methylation efficiencies.

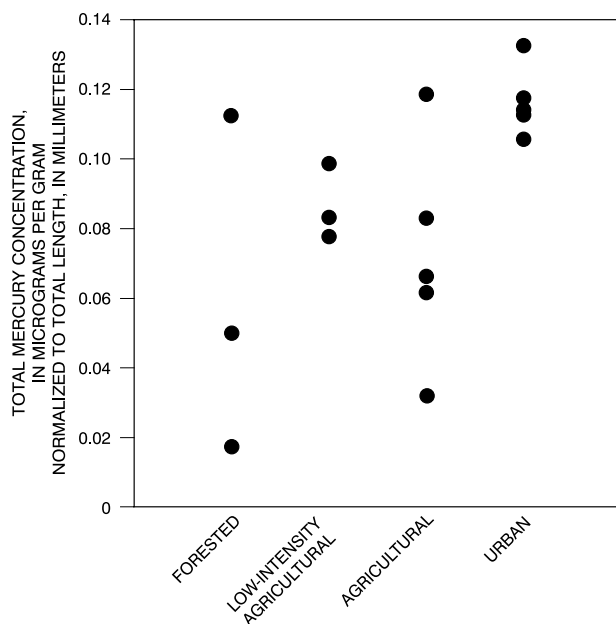
### Differences among land-use groups

After studying occurrence and distribution of Hg in the basin as a whole, comparisons were made among sites grouped according to land use to determine which processes may affect the distribution of Hg within each group. All the forested and two of the three low intensity-agricultural basins are in the northern Appalachian region of

the study area, and most urban basins are in the southern area. Agricultural basins span the entire study area, but most moderate to high agricultural land-use basins are in the middle and southern sections of the study area. Mixed land-use sites and large-river sites were not included in this analysis because of the multiplicity of land uses within each basin.

The urban sites had the highest median concentration of tHg (length-normalized) in smallmouth bass (fig. 16). Next were the low-intensity agricultural group, the agricultural group, and the forested group. The forested and agricultural basins had greater ranges in tHg fillet concentrations than the other two land-use groups (fig. 16).

Some land-use differences were observed in concentrations of tHg, MeHg, and the methylation efficiency in streamwater and bed-sediment samples (fig. 17A, 17B, and 17C, respectively). The urban land-use group had the highest tHg concentrations in streamwater and bed-sediment samples (fig. 17A). No patterns could be determined in concentrations of MeHg (fig. 17B). Methylation efficiency was lower in the urban group than the other groups (fig. 17C).



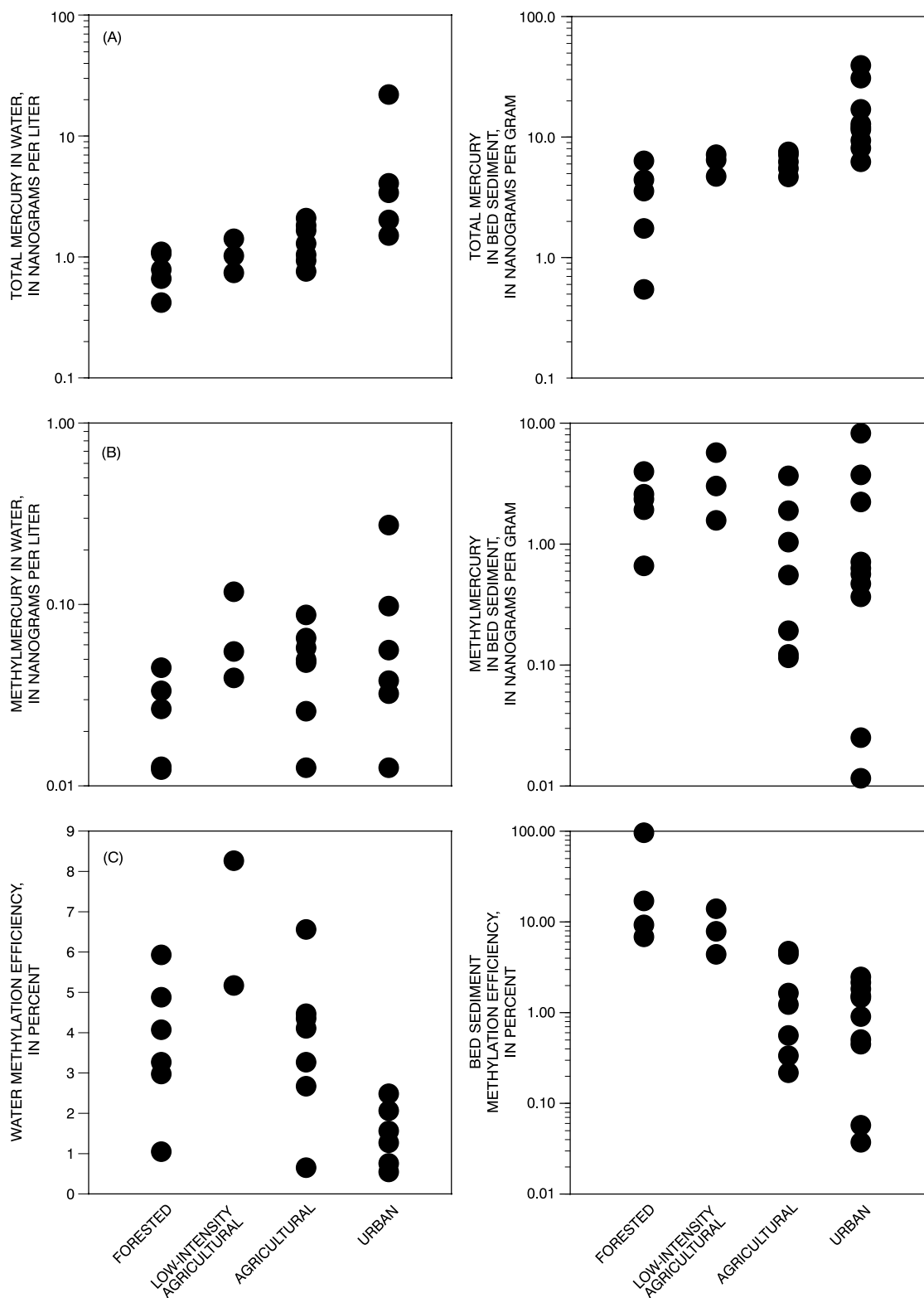
**Figure 16.** Distribution of total mercury concentrations in smallmouth bass fillets by land-use groups within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

Correlation analyses were used to determine the factors affecting Hg in fillets, streamwater, and bed-sediment samples among the different land-use groups (table 6). Sites from the forested and low intensity-agricultural groups were combined into a 'forested/low intensity-agricultural' group to provide a greater number of sites for data analysis. These results (table 6) suggest that each land-use group had different environmental factors affecting Hg concentrations in fish, water, and bed sediments. More data are needed within each land-use group to better characterize these factors.

Within the forested/low-intensity agricultural group, increased urbanization was associated with decreased tHg concentrations in smallmouth bass (length-normalized). Increased population density was associated with decreased methylation efficiency in bed sediment. Increased agricultural land cover was associated with increased concentrations of tHg (normalized to LOI) in bed sediment and increased methylation efficiency in water. Increased agricultural land cover also was associated with decreased MeHg concentrations in water, and methylation efficiency in bed sediment is observed to increase with an increase in agricultural land cover (table 6). Methylation efficiency in bed sediment also was negatively correlated with sulfate concentration.

Within the agricultural group, increased urbanization (denoted as urban land cover), impervious land surface, and population density were associated with increased tHg concentrations in smallmouth bass (length-normalized) (table 6). Increased septic-tank density was associated with decreased tHg concentrations in water (possibly reflecting the lower septic-tank density in towns and villages served by wastewater treatment plants). Increased elevation was associated with decreased methylation efficiency in the water.

Within the urban group, increased forested land cover and wetland cover were associated with an increase in tHg concentration in smallmouth bass (length-normalized). Concentrations in smallmouth bass fillets were not significantly correlated with water or bed sediment tHg, MeHg, or methylation efficiency. Furthermore, no forms of Hg in fish, water, or bed sediment exhibited a significant correlation with pH, DOC, or sulfate concentration.



**Figure 17.** Distribution of streamwater and bed sediment forms of mercury (A) total mercury, (B) methylmercury, and (C) methylation efficiency, by land-use groups within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001.

**Table 6.** Results of Kendall Tau correlation analyses among forms of mercury in fish fillets, streamwater, and bed-sediment samples, and environmental and landscape variables, within forested/low intensity-agricultural, agricultural, and urban land-use classes for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

[LOI, Loss-On-Ignition; \*\*\*,  $p \leq 0.001$ ; \*\*,  $p \leq 0.01$ ; \*,  $p = 0.05$ ; ns, not significant ( $p > 0.05$ ). Only factors with one or more significant correlations are shown. Numbers of observations are shown in parentheses.]

Environmental and landscape variables	Mercury in smallmouth bass fillets, normalized to mean total length	Total mercury		Methylmercury		Methylation efficiency	
		Water	Bed sediment (LOI normalized)	Water	Bed sediment (LOI normalized)	Water	Bed sediment (LOI normalized)
Forested / low-intensity agricultural group							
Urban land cover <sup>1</sup>	-0.73* (6)	ns (8)	ns (8)	ns (8)	ns (8)	ns (8)	ns (8)
Estimated population density 1997 <sup>2</sup>	ns (6)	ns (8)	ns (8)	ns (8)	ns (8)	ns (8)	-0.57 (8)
Forest land cover <sup>1</sup>	ns (6)	ns (8)	-0.64** (8)	-0.76** (8)	-0.76* (8)	-0.71** (8)	ns (8)
Agricultural land cover <sup>1</sup>	ns (6)	ns (8)	.93** (8)	-.76** (8)	ns (8)	.71** (8)	-.57 (8)
Septic-tank density (1990) <sup>2</sup>	ns (6)	ns (8)	ns (8)	ns (8)	.81* (8)	ns (8)	ns (8)
Drainage area	ns (6)	ns (8)	ns (8)	ns (8)	.81* (8)	ns (8)	ns (8)
Sulfate	ns (6)	ns (8)	ns (8)	ns (8)	ns (8)	ns (8)	-.64 (8)
Agricultural group							
Urban land cover <sup>1</sup>	.73* (6)	ns (7)	ns (8)	ns (7)	ns (7)	ns (7)	ns (7)
Impervious land surface <sup>1</sup>	.73* (6)	ns (7)	ns (8)	ns (7)	ns (7)	ns (7)	ns (7)
Population density 1997 <sup>2</sup>	.87* (6)	ns (7)	ns (8)	ns (7)	ns (7)	ns (7)	ns (7)
Septic-tank density (1990) <sup>2</sup>	ns (6)	-0.81** (7)	ns (8)	ns (7)	ns (7)	ns (7)	ns (7)
Elevation	ns (6)	ns (7)	ns (8)	ns (7)	ns (7)	-.62* (7)	ns (7)
Urban group							
Forest land cover <sup>1</sup>	.80* (5)	ns (6)	ns (10)	ns (7)	ns (10)	ns (6)	ns (10)
Wetland cover <sup>1</sup>	.80* (5)	ns (6)	ns (10)	ns (7)	ns (10)	ns (6)	ns (10)

<sup>1</sup> U.S. Geological Survey, 1992.

<sup>2</sup> U.S. Department of Commerce, 1990.

### Comparison of Results With the National Mercury Pilot Program and Other Studies

Concentrations of tHg in fish fillets from the Delaware River Basin ranked eighth highest (geometric mean; 0.26  $\mu\text{g/g}$ ) of the 20 basins in the NMPP (Brumbaugh and others, 2001). The highest geometric mean was in the Nevada Basin and Range NAWQA study basin of Nevada and California (geometric mean, 3.34  $\mu\text{g/g}$ ) and the lowest was in Oahu Island, Hawaii, NAWQA study basin (geometric mean; 0.03  $\mu\text{g/g}$ ). These results, however, were calculated before this study was completed. The recalculated geometric mean for the Delaware River Basin is 0.17  $\mu\text{g/g}$ , which would rank the basin around twelfth highest instead of eighth highest.

Results of the NMPP indicate that tHg concentrations in fish fillets (length-normalized) increased with latitude, percent wetland, and the methylation efficiency of bed sediment (Brumbaugh and others, 2001). The Delaware study had

the opposite results. If the Delaware study had more data and larger ranges within each category tested, similar to NMPP, maybe the results would have been similar between the two studies. The percentage of wetland in the Delaware River Basin ranged from 0 to 18, but the NMPP had a range of 0 to 50 (Brumbaugh and others, 2001). Within the Delaware River Basin, the percentage of wetland in a given stream basin was estimated from satellite images.

Concentrations of tHg in fish correlated with tHg concentrations in bed sediment, in contrast to the lack of correlation observed in the NMPP study (Brumbaugh and others, 2001). Several other studies also have seen the same relation between MeHg concentrations in bed sediment to concentrations of Hg in fish (Burns and others, 1997; U.S. Environmental Protection Agency, 1997; Australian and New Zealand Environment and Conservation Council, 2000a; New York State Department of Environmental Conservation, 2002). This differ-

ence between NMPP and the Delaware River Basin could be because of the greater percentage of urban sites in the Delaware River Basin study as compared with NMPP. This difference also could be related to differences in deposition, or habitat, diet and uptake dynamics between smallmouth bass used for analysis in the Delaware River Basin and largemouth bass (*Micropterus salmoides*) used in the NMPP. The largemouth bass tHg concentrations correlated with MeHg in water and was the strongest influential variable on Hg concentration in fish noted in the NMPP (Brumbaugh and others, 2001).

Alkalinity and pH of the streams showed no significant relation with Hg in fish tissue. Many lake studies have found that Hg concentrations in fish are often inversely related to lake alkalinity or pH (Watras and Huckabee, 1994; Watras and Bloom, 1992; Spry and Wiener, 1991; Cope and others, 1990). However, this is not true for all lakes. In Little Rock Lake, Wis., for example, when calcium concentrations increased, the rate of MeHg uptake across the fish's gill-membrane increased (Wiener and others, 1990). The calcium shift occurred when the pH was adjusted. Without the shift in calcium, the effect of pH on uptake of Hg by the fish in this lake is unclear. Another study conducted by Rodgers and others (1987) showed that MeHg uptake by rainbow trout and walleye did not differ among three different pH levels used in the study. Little is known about the relation between pH and the uptake of Hg by fish in flowing waters.

Other studies have shown a correlation between DOC and the uptake of Hg by fish (U.S. Geological Survey, 1995; Krabbenhoft and others, 1999; U.S. Department of Interior, 1998; U.S. Environmental Protection Agency, 2000b). Above a threshold DOC concentration, bioaccumulation of Hg in fish appears to decrease (U.S. Department of Interior, 1998; U.S. Environmental Protection Agency, 2000b). However, in the Delaware River Basin, only a weak correlation between DOC and tHg concentrations in water was observed (table 4). The low median and relatively narrow range of DOC concentrations among the Delaware River Basin sites (median 2.1 ng/L, minimum 0.7 ng/L, and maximum 9.5 ng/L) may account for the lack of correlation. A 74-percent decrease in MeHg uptake rate across the gills of Sacramento blackfish (*Orthodon microlepidotus*) when 2 mg/L DOC were present in the water was reported by the National Center for Environmental Research (2002).

Weight, length, and age of the fish are highly correlated with Hg concentrations in fish tissue (Braune, 1987; Cope and others, 1990; Stahl and Sobat, 2000; Huggett and others, 2001). The Delaware River Basin studies focused on fish in the 2- to 3-year age range to allow stronger correlations to be made between the environmental variables and Hg concentrations in fish rather than with fish age and size.

Water temperature can be an important variable for uptake of Hg by fish. As water temperatures increase, bioaccumulation of Hg in fish filets increases (Australian and New Zealand Environment and Conservation Council, 2000b) because of increased metabolic activity and increased Hg methylation efficiency. The temperature data collected as part of the Delaware River Basin study were collected during August and September, and little or no temperature variation was observed that would account for slower or faster uptake of Hg by the smallmouth bass analyzed.

A USEPA study (1997) indicated that the Delaware River Basin has one of the highest deposition rates of Hg in the country; estimated atmospheric deposition rates of Hg are in excess of 20 mg/m<sup>2</sup>/yr. Although methylation efficiency in the Delaware River Basin is relatively low, Hg concentrations in fish are relatively high. In the Delaware River Basin, precipitation rates are higher at the forested sites compared to the rest of the basin (Fischer, 1999). However, Pilgrim and others (1999) studied atmospheric deposition rates of Hg in forested and unforested areas and the concentration of Hg in fish. They determined no significant difference in atmospheric deposition or fish Hg concentrations between the two areas.

In the Delaware River Basin, fish tissue from the urban sites had the highest median concentration of tHg of the four groups in the study, and fish from the forested group had the lowest tHg concentrations. These results differ from those of NMPP, in which the lowest median tHg concentration in fish tissue was from sites in the urban group, and the highest was in the forested/low-intensity agricultural group (Brumbaugh and others, 2001).

With no apparent patterns observed in the present study among the land-use groups for MeHg concentrations, no comparisons with NMPP results were possible. The NMPP found that the MeHg concentrations in water were highest at forested/low-intensity agricultural sites and lowest at

urban sites (Krabbenhof and others, 1999), and MeHg concentrations in bed sediment were highest at the forested/low-intensity agricultural sites, the urban sites were next, and the agricultural sites had the lowest MeHg concentrations.

The methylation efficiency pattern observed in the Delaware study is similar to what was observed in the NMPP. Both studies showed higher methylation efficiencies in streams flowing through mixed forested and agricultural landscapes than in streams flowing through urban landscapes (Krabbenhof and others, 1999).

Both studies suggest that regional and land-use factors are important in affecting the processing and bioavailability of Hg in the environment. High tHg concentrations in fish tissue and bed sediment are related to factors associated with urban landscapes. Human effects such as increased concentrations of tHg in fish tissue are observed as population density increases in urban areas of the Delaware River Basin. The source of the higher tHg fish-tissue concentrations observed in the forested areas could not be determined but may have to do with the higher amounts of rainfall in the area. Additional study with a larger number of sites using the urban gradient for site-selection purposes would be helpful in determining whether the urbanization effect is real or an artifact of a small number of sampling sites.

## SUMMARY AND CONCLUSIONS

The nontidal part of the Delaware River Basin has been studied as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program to integrate physical, chemical, and biological sampling efforts to determine the status and trends in surface- and groundwater resources. The Delaware River Basin also was included in the USGS National Mercury Pilot Program (NMPP).

Fish species collected as part of the Delaware River Basin study included smallmouth bass (*Micropterus dolomieu*), brown trout (*Salmo trutta*), chain pickerel (*Esox niger*), largemouth bass (*Micropterus salmoides*), and rock bass (*Ambloplites rupestris*). Only total mercury (tHg) was analyzed in this study. The U.S. Environmental Protection Agency human-health criteria of 0.3 µg/g wet-weight mercury (Hg) concentrations in fillets was exceeded in 7 of the 32 fillet samples collected from 31 sites. With the exception of two samples collected in forested areas of the basin, these samples

were collected from streams near the major cities within the basin. The U.S. Fish and Wildlife Service fish-eating bird and wildlife criterion of 0.1 µg/g wet weight in whole fish was exceeded in 27 of 32 samples. Although comparing concentrations from fish fillets is not a truly valid comparison to a criterion established for whole fish, the fillets had higher levels of Hg than are safe for wildlife.

Correlation analyses were completed comparing concentrations of Hg in smallmouth bass (length-normalized) with water and bed sediment tHg and methylmercury (MeHg) concentrations, methylation efficiencies, and other environmental variables. Only percent impervious surface and tHg concentration in bed sediment correlated with Hg concentrations in the smallmouth bass.

A subgroup of the fish sites was analyzed with the environmental variables. This subgroup consisted of sites where the population was greater than or equal to 100 people per square mile. Within this group of sites, population density, urban land cover, impervious surface, and bed sediment tHg concentrations were positively correlated with tHg concentrations in smallmouth bass fillets. Wetland cover, percent septic systems, elevation, latitude, and bed sediment methylation efficiency were negatively correlated with tHg concentrations in smallmouth bass fillets. These correlations all indicate an urban effect on Hg concentrations in smallmouth bass fillets.

Concentrations of tHg and MeHg in water in the more urbanized areas of the Delaware River Basin were higher than in other areas. Concentrations of tHg were positively correlated with urbanization factors and negatively correlated with forested land cover. No correlations were noted for concentrations of MeHg with any factors in this study. Methylation efficiency was negatively correlated with urbanization.

Concentrations of tHg in bed sediments in the urbanized area of the basin were higher than in other areas, and concentrations of MeHg in the northern (more forested) area of the basin were higher than in other areas. Urbanization was positively correlated with tHg concentration in bed sediments; forested land cover and elevation were negatively correlated. Forested land cover was positively correlated with bed sediment MeHg concentrations. Methylation efficiency in bed sediment was higher in the forested areas and was negatively correlated with urbanization, similar to methylation efficiency in water.



There are several different land-use groups within the Delaware River Basin—urban, agricultural, low-intensity agricultural, and forested. Correlations within each group were analyzed to determine if different environmental variables played a role in fillet Hg concentrations among the four groups. The fillets from urban sites had the highest median concentration of tHg, followed by low-intensity agricultural sites, the agricultural sites, and the forested sites. Forested land cover and wetland cover correlated positively with Hg concentrations in fillets within the urban group. The Hg fillet concentrations in the agricultural group were positively correlated with urbanization factors (population, urban land cover, and impervious land), whereas forested and low-intensity agricultural groups had fillet Hg concentrations that were negatively correlated with urbanization.

Concentrations of tHg in water from sites in the agricultural group were negatively correlated with septic-tank density, and methylation efficiency was negatively correlated with elevation. In the forested and low-intensity agricultural groups, MeHg concentrations were negatively correlated with forested land and agricultural land cover. Methylation efficiency in the forested and low-intensity agricultural group was negatively correlated with forested land cover and positively

correlated with agricultural land cover. No significant correlations for tHg, MeHg, or methylation efficiency were noted for the urban group.

Concentrations of tHg in bed sediment were positively correlated with agricultural land cover and negatively correlated with forested land cover in the forested and low-intensity agricultural groups. Concentrations of MeHg in bed sediment from the forested and low-intensity agricultural groups were positively correlated with septic-tank density and basin drainage area and negatively correlated with forested land cover. Methylation efficiency in forested and low-intensity agricultural sites was negatively correlated with population density, agricultural land cover, and sulfate concentration in the water. Bed sediment tHg concentrations in urban sites were not significantly correlated with any environmental variables tested as part of the study.

All three media—fish, water, and bed sediments—reflected an urbanization effect, but the relation for each was different. Because of the limited number of samples, neither concentrations of MeHg in streamwater nor bed sediment were good predictors of tHg concentrations in smallmouth bass in the Delaware River Basin. Additional sampling would be needed to draw more precise conclusions.

## REFERENCES CITED

- Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand, 2000a, National water quality management strategy—Australian and New Zealand guidelines for fresh and marine water quality—Aquatic ecosystems—Rationale and background information: Australia and New Zealand, Paper no. 4, v. 2, chap. 8, p. 8.3/128-132.
- 2000b, National water quality management strategy—Australian and New Zealand guidelines for fresh and marine water quality—Primary industries—Rationale and background information: Australia and New Zealand, Paper no. 4, v. 3, chap. 9, p. 9.4/43.
- Bahnick, D., and Sauer, C., 1994, A national study of mercury contamination of fish—IV—Analytical methods and results: *Chemosphere*, v. 29, no. 3, p. 537-546.
- Bilger, M.D., Brightbill, R.A., and Campbell, H.L., 1999, Occurrence of organochlorine compounds in whole fish tissue from streams of the lower Susquehanna River Basin, Pennsylvania and Maryland, 1992: U.S. Geological Survey Water-Resources Investigations Report 99-4065, 17 p.
- Braune, B.M., 1987, Mercury accumulation in relation to size and age of Atlantic Herring (*Clupea harengus harengus*) from the southwestern bay of Fundy, Canada: *Archives of Environmental Contamination and Toxicology*, v. 16, p. 311-320.
- Brumbaugh, W.G., Krabbenhoft, D.P., Helsel, D.R., Wiener, J.G., and Echols, K.R., 2001, A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients—Bioaccumulation in fish: U.S. Geological Survey, USGS/BRD/BSR-2001-0009, 28 p.
- Burns, T.P., Hadden, C.T., Cornaby, B.W., and Mitz, S.V., 1997, A food web model of mercury transfer from stream sediment to predators of fish for ecological risk based clean-up goals: American Society for Testing and Materials, ASTM STP 1317, p. 7-27.
- Cope, W.G., Wiener, J.G., and Rada, R.G., 1990, Mercury accumulation in yellow perch in Wisconsin seepage lakes—Relation to lake characteristics: *Environmental Toxicology and Chemistry*, v. 9, p. 931-940.
- Eisler, Ronald, 1987, Mercury hazards to fish, wildlife, and invertebrates—A synoptic review: U.S. Fish and Wildlife Service Biological Report 85, v. 1, no. 10, 90 p.
- Fischer, J.M., 1999, National Water-Quality Assessment Program—Delaware River Basin: U.S. Geological Survey Fact Sheet FS-056-99, 6 p.
- Fitzgerald, W.F., and Watras, C.J., 1989, Mercury in surficial waters of rural Wisconsin lakes: *Science of the Total Environment*, v. 87/88, p. 223-232.
- Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.
- Goldstein, R.M., Brigham, M.E., and Stauffer, J.C., 1996, Comparison of mercury concentrations in liver, muscle, whole bodies, and composites of fish from the Red River of the North: *Canadian Journal of Fisheries and Aquatic Sciences*, v. 53, p. 244-252.
- Gurtz, M.E., 1994, Design of biological components of the National Water-Quality Assessment (NAWQA) Program in Loeb, S.L., and Spacie, A., eds., *Biological monitoring of aquatic systems*: Boca Raton, Fla., Lewis Publishers, p. 323-354.
- Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for National Water-Quality Assessment Program: U.S. Geological Survey Circular 1021, 42 p.
- Horvat, M., Bloom, N.S., and Liang, L., 1993, Comparison of distillation with other current isolation methods for the determination of methylmercury compounds in low level environmental samples, Part I, Sediment: *Analytica Chimica Acta*, v. 281, p. 135-152.
- Huggett, D.B., Stevens, J.A., Allgood, J.C., Lutken, C.B., Grace, C.A., and Benson, W.H., 2001, Mercury in sediment and fish from North Mississippi Lakes: *Chemosphere*, v. 42, p. 923-929.

## REFERENCES CITED—CONTINUED

- Krabbenhoft, D.P., Wiener, J.G., Brumbaugh, W.G., Olson, M.L., DeWilde, J.F., and Sabin, T.J., 1999, A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients: U.S. Geological Survey Water-Resources Investigations Report 99-4018-B, 13 p.
- Leahy, P.P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 90-174, 10 p.
- Leahy, P.P., and Wilber, W.G., 1991, National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 91-54, 2 p.
- MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: Archives of Environmental Contamination and Toxicology, v. 39, p. 20-31.
- McMahon, Gerard, and Cuffney, T.F., 2000, Quantifying urban intensity in drainage basins for assessing stream ecological conditions: Journal of the American Water Resources Association, v. 36, p. 1,247-1,261.
- National Center for Environmental Research, 2002, Progress Report—Mercury uptake by fish: U.S. Environmental Protection Agency, Office of Research and Development, accessed April 17, 2002, at <http://es.epa.gov/ncer/progress/centers/cehr/aqua1apr.html>
- National Research Council, 2000, Toxicological effects of methylmercury: Washington, D.C., National Academy Press, 344 p.
- New York State Department of Environmental Conservation, 2002, Mercury management in New York State: accessed January 31, 2002, at <http://www.dec.state.ny.us/website/dshlm/redrecy/mercury.htm>
- Olson, M.L., Cleckner, L.B., Hurley, J.P., Krabbenhoft, D.P., and Heelan, T.W., 1997, Resolution of matrix effects on analysis of total and methylmercury in aqueous samples from the Florida Everglades: Fresenius Journal of Analytical Chemistry, v. 358, p. 392-396.
- Olson, M.L., and DeWild, J.F., 1999, Low-level techniques for the collection and species-specific analysis of low levels of mercury in water, sediment, and biota, in Morganwalp, D.W., and Buxon, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the technical meeting, Charleston, S.C., March 8-12, 1999, v. 2, Contamination of hydrologic systems and related ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018-B, 8 p.
- Pilgrim, Wilfred, Lucotte, Marc, Montgomery, Shelagh, Santos-Burgoa, Carlos, Uriarte, M.I.I., Abascal-Garrido, Francisco, Round, Margaret, and Porcella, Don, 1999, Meeting the challenges of continental pollutant pathways—Mercury—Case study: Environment Canada, Final Report to the Secretariat of the CEC, accessed April 17, 2002, at [http://www.eman-rese.ca/eman/reports/publications/99\\_mercurywkshp/page4.html](http://www.eman-rese.ca/eman/reports/publications/99_mercurywkshp/page4.html)
- Rodgers, D.W., Watson, T.A., Langan, J.S., and Wheaton, T.J., 1987, Effects of pH and feeding regime on methylmercury accumulation within aquatic microcosms: Environmental Pollution, v. 45, p. 261-274.
- Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-0458, p. 20.
- Spry, D.J., and Wiener, J.G., 1991, Metal bioavailability and toxicity to fish in low-alkalinity lakes—A critical review: Environmental Pollution, v. 71, p. 243-304.
- Stahl, J.R., and Sobat, S.L., 2000, Creek chub as sentinel indicator species for relative regional assessment of mercury contamination and monitoring pollutant trends in Indiana rivers and streams: Indiana Department of Environmental Management, IDEM/32/002/2000, 25 p.
- U.S. Department of Commerce, 1990, United States Census 1990: U.S. Census Bureau, accessed 1997, at <http://www.census.gov>

## REFERENCES CITED—CONTINUED

- U.S. Department of Interior, 1998, Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment—Mercury: National Irrigation Water Quality Program Information Report, no. 3, 22 p.
- U.S. Environmental Protection Agency, 1997, Mercury study report to congress - Volume III - Fate and transport of mercury in the environment: Office of Air Quality Planning and Standards, Office of Research and Development, EPA-451/R-97-005, 243 p. + appendices.
- \_\_\_\_\_, 2000a, Update - National listing of fish and wildlife advisories: USEPA Office of Water, EPA-823-F-00-016, 6 p.
- \_\_\_\_\_, 2000b, Mercury transport and fate in watersheds: National Center for Environmental Research, Star Report 10, 8 p.
- \_\_\_\_\_, 2001a, Methylmercury: EPA-823-F-01-001, accessed November 11, 2001, at <http://www.epa.gov/waterscience/criteria/methylmercury/factsheet.html>
- \_\_\_\_\_, 2001b, Mercury—General information—Frequently asked questions: accessed May 3, 2001, at <http://www.epa.gov/mercury/information.htm#questions>
- \_\_\_\_\_, 2002, 2002 Edition of the drinking water standards and health advisories: Washington, D.C., Office of Water, EPA 822-R-02-038, p. 19.
- U.S. Geological Survey, 1992, National Land Cover Characterization, accessed 1997, at <http://landcover.usgs.gov/natl/landcover.html>
- \_\_\_\_\_, 1995, Mercury contamination of aquatic ecosystems: U.S. Geological Survey Fact Sheet, FS-261-95.
- Wachs, B., 1985, Bioindicators for the heavy metal load of river ecosystems: Symposia Biologica Hungarica, v. 29, p. 179-190.
- Watras, C.J., and Bloom, N.S., 1992, Mercury and methylmercury in individual zooplankton—Implications for bioaccumulation: Limelight and Oceanography, v. 37, p. 1,313-1,318.
- Watras, C.J., and Huckabee, J.W., eds., 1994, Mercury pollution integration and synthesis: Boca Raton, Fla., Lewis Publishers, p. 153-177.
- Wiener, J.G., Fitzgerald, W.F., Watras, C.J., and Rada, R.G., 1990, Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake: Environmental Toxicology and Chemistry, v. 9, p. 909-918.

**Appendix.** Site information, sampling years, fish species, number of fish per sample, mercury and (or) methylmercury concentrations in fish, streamwater and bed sediment, and Loss-On-Ignition for bed sediment for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001

[µg/g, micrograms per gram; ng/L, nanograms per liter; ng/g, nanograms per gram; LOI, Loss-On-Ignition; —, no data]

Site name	U.S. Geological Survey identification number	Latitude	Longitude	Year of fillet sample	Total mercury in fish fillets - wet weight (µg/g)	Fish species	Number of fish per sample	Year of water sample	Total mercury in water (ng/L)	Methyl mercury in water (ng/L)	Year of bed sediment sample	Total mercury in bed sediment (ng/g)	Methyl mercury in bed sediment (ng/g)	LOI for bed sediment (ng/g)
Raccoon Creek near Swedesboro, N.J.	01477120	394428	751533	<sup>1</sup> 1998	0.29	Chain pickerel	1	<sup>1</sup> 1998	1.1	0.05	<sup>1</sup> 1998	34	0.20	4.5
Cooper River at Haddonfield, N.J.	01467040	395411	750119	<sup>1</sup> 1999	.21	Largemouth bass	3	<sup>1</sup> 1999	—	.04	<sup>1</sup> 1999	140	.73	9.9
Darby Creek near Darby, Pa.	01475510	395544	751622	<sup>1</sup> 1999	.35	Smallmouth bass	2	<sup>1</sup> 1999	3.5	.06	<sup>1</sup> 1999	91	2.3	7.3
Ridley Creek near Media, Pa.	01476470	395557	752442	<sup>2</sup> 2001	.31	Rock bass	3	<sup>1</sup> 1998	.86	—	2000	44	—	4.3
South Branch Pennsauken Creek at Cherry Hill, N.J.	01467081	395630	750005	<sup>1</sup> 1999	.09	Largemouth bass	4	—	—	—	1999	34	.65	4.0
Schuylkill River at Philadelphia, Pa.	01474500	395804	751120	<sup>1</sup> 1998	.32	Smallmouth bass	5	—	—	—	—	—	—	—
North Branch Rancocas Creek at Pemberton, N.J.	01467000	395810	744105	—	—	—	—	—	—	—	<sup>1</sup> 1999	29	1.2	5.2
Crum Creek at Goshen Road near Whitehorse, Pa.	01475845	395924	752616	—	—	—	—	<sup>1</sup> 1998	1.1	.04	<sup>1</sup> 2000	25	.07	4.5
Darby Creek at Foxcroft, Pa.	01475430	395945	752121	<sup>2</sup> 2001	.19 .22	Smallmouth bass Rock bass	1 2	<sup>1</sup> 1999	2.1	<.02	<sup>1</sup> 2000	58	.03	4.7
Wissahickon Creek below Walnut Lake near Manayunk, Pa.	01473990	400150	751154	<sup>1</sup> 1999	.34	Smallmouth bass	1	<sup>1</sup> 1999	1.6	.03	<sup>1</sup> 1999	240	3.9	7.7
East Branch Brandywine Creek near Dorlan, Pa.	01480665	400308	754328	<sup>2</sup> 2001	.14	Smallmouth bass	2	<sup>1</sup> 1998	.80	.03	<sup>1</sup> 2000	34	.12	6.9
Stony Creek at Steriger Street at Norristown, Pa.	01473470	400738	752043	<sup>2</sup> 2001	.21	Smallmouth bass	3	<sup>1</sup> 1998	1.6	<.02	<sup>1</sup> 2000	20	.01	3.0
Pennypack Creek at Paper Mill, Pa.	01467040	400824	750428	<sup>1</sup> 1999	.13	Rock bass	3	—	—	—	<sup>1</sup> 1999	29	.48	3.0
French Creek near Phoenixville, Pa.	01472157	400905	753606	<sup>1</sup> 1999	.20	Smallmouth bass	3	<sup>1</sup> 1999	1.8	.05	<sup>1</sup> 1999	78	3.8	13
Pigeon Creek at Parker Ford, Pa.	01472100	401148	753513	<sup>2</sup> 2001	.15	Smallmouth bass	1	—	—	—	<sup>1</sup> 2000	16	—	2.0
Delaware River at Trenton, N.J.	01463500	401318	744642	<sup>1</sup> 1998	.29	Smallmouth bass	5	—	—	—	—	—	—	—
Little Neshaminy Creek at Valley Road near Neshaminy, Pa.	01464907	401345	750712	<sup>1</sup> 1998	.27	Smallmouth bass	2	<sup>1</sup> 1998	4.1	.10	<sup>1</sup> 1998	40	.38	3.0
Hay Creek near Birdsboro, Pa.	01471668	401504	754850	<sup>1</sup> 1998	.33	Smallmouth bass	1	<sup>1</sup> 1998	.77	.04	<sup>1</sup> 1998	36	1.6	5.4
Shabakunk Creek near Lawrenceville, N.J.	01463810	401519	744417	<sup>2</sup> 2001	.20	Rock bass	2	<sup>1</sup> 1998	22	.28	<sup>1</sup> 2000	120	.58	7.0
Manatawny Creek near Pottstown, Pa.	01471980	401622	754049	<sup>1</sup> 1998	.17	Smallmouth bass	3	<sup>1</sup> 1998	1.4	.06	<sup>1</sup> 1998	63	1.1	8.5

**Appendix.** Site information, sampling years, fish species, number of fish per sample, mercury and (or) methylmercury concentrations in fish, streamwater and bed sediment, and Loss-On-Ignition for bed sediment for sites within the Delaware River Basin, New Jersey, New York, and Pennsylvania, 1998 through 2001—Continued

[µg/g, micrograms per gram; ng/L, nanograms per liter; ng/g, nanograms per gram; LOI, Loss-On-Ignition; —, no data]

Site name	U.S. Geological Survey identification number	Latitude	Longitude	Year of fillet sample	Total mercury in fish filets - wet weight (µg/g)	Fish species	Number of fish per sample	Year of water sample	Total mercury in water (ng/L)	Methyl mercury in water (ng/L)	Year of bed sediment sample	Total mercury in bed sediment (ng/g)	Methyl mercury in bed sediment (ng/g)	LOI for bed sediment (ng/g)
Pine Run at Chalfont, Pa.	01464710	401720	751211	—	—	—	—	<sup>1</sup> 1998	13	0.06	<sup>1</sup> 2000	49	0.21	7.7
Wyomissing Creek at West Reading, Pa.	01471520	401941	755641	<sup>1</sup> 1999	0.03	Brown trout	2	—	—	—	<sup>1</sup> 1999	380	8.7	9.4
Pidcock Creek near New Hope, Pa.	01462100	401946	745614	—	—	—	—	<sup>1</sup> 1998	1.0	<.07	<sup>1</sup> 2000	56	.13	9.6
Tulpehocken Creek near Bernville, Pa.	01470779	402448	761019	<sup>1</sup> 1998	.24	Smallmouth bass	1	<sup>1</sup> 1998	2.1	.09	<sup>1</sup> 1998	46	.57	6.5
Little Lehigh Creek near East Texas, Pa.	01451425	403234	753347	<sup>1</sup> 1998	.03	Brown trout	3	—	—	—	—	—	—	—
Jordan Creek near Schnecksville, Pa.	01451800	403942	753738	<sup>1</sup> 1999	.06	Smallmouth bass	3	<sup>1</sup> 1999	1.9	<.02	<sup>1</sup> 1999	43	2.0	6.4
Lehigh River at Glendon, Pa.	01454700	404009	751412	<sup>1</sup> 1998	.13	Smallmouth bass	5	—	—	—	—	—	—	—
Brodhead Creek at Stroudsburg, Pa.	01442500	405914	751102	<sup>1</sup> 1999	.06	Smallmouth bass	2	<sup>1</sup> 1999	1.1	.05	<sup>1</sup> 1999	33	2.4	5.1
Bush Kill Creek at Bushkill, Pa.	01439500	410517	750042	<sup>1</sup> 1999	.13	Smallmouth bass	2	<sup>1</sup> 1999	.82	.03	<sup>1</sup> 1999	24	4.1	13
Flat Brook near Flatbrookville, N.J.	01440000	410624	745709	<sup>1</sup> 1999	.33	Smallmouth bass	2	<sup>1</sup> 1999	.69	.03	<sup>1</sup> 1999	7.2	.68	1.6
Delaware River at Port Jervis, N.Y.	01434000	412214	744152	<sup>1</sup> 1998	.33	Smallmouth bass	4	—	—	—	—	—	—	—
Neversink River near Godeffroy, N.Y.	01437500	412628	743608	<sup>1</sup> 1999	.18	Rock bass	2	<sup>1</sup> 1999	1.2	<.03	<sup>1</sup> 1999	27	2.6	7.2
Lackawaxen River at Hawley, Pa.	01431500	412834	751021	<sup>1</sup> 1999	.18	Smallmouth bass	2	<sup>1</sup> 1999	1.1	.06	<sup>1</sup> 1999	38	3.1	7.7
Neversink River near Claryville, N.Y.	01435000	415324	743525	<sup>1</sup> 1999	.12	Brown trout	2	<sup>1</sup> 1999	.43	<.03	<sup>1</sup> 1999	1.5	2.0	2.6
W. Br. Delaware River at Walton, N.Y.	01423000	420958	750825	<sup>1</sup> 1999	.15	Smallmouth bass	2	<sup>1</sup> 1999	1.4	.12	<sup>1</sup> 1999	40	5.9	5.4

<sup>1</sup> Analyzed at the U.S. Geological Survey Wisconsin Mercury Research Laboratory.

<sup>2</sup> Analyzed at the U.S. Geological Survey National Water Quality Laboratory.